Corrosion resistant metallic glasses for biosensing applications

Ariane Sagasti, Ana Catarina Lopes, Andoni Lasheras, Verónica Palomares, Javier Carrizo, Jon Gutierrez, and J. Manuel Barandiaran

Citation: AIP Advances **8**, 047702 (2018); doi: 10.1063/1.4994108
View online: https://doi.org/10.1063/1.4994108
View Table of Contents: http://aip.scitation.org/toc/adv/8/4
Published by the American Institute of Physics

AIP ADVANCES **8**, 047702 (2018)

Corrosion resistant metallic glasses for biosensing applications

Ariane Sagasti,[1,a] Ana Catarina Lopes,[1] Andoni Lasheras,[2] Verónica Palomares,[3] Javier Carrizo,[4] Jon Gutierrez,[1,2] and J. Manuel Barandiaran[1,2]
[1]*BCMaterials, Ibaizabal Bidea, Edificio 500, Parque Tecnológico de Bizkaia, Derio 48160, Spain*
[2]*Dept. of Electricity and Electronics, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Faculty of Science and Technology, P. Box 644, 48080 Bilbao, Spain*
[3]*Dept. of Inorganic Chemistry, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Faculty of Science and Technology, P. Box 644, 48080 Bilbao, Spain*
[4]*Dept. of Physics, Universidad de Oviedo, Calvo Sotelo s/n, 33007 Oviedo, Spain*

(Received 4 July 2017; accepted 16 July 2017; published online 12 October 2017)

We report the fabrication by melt spinning, the magnetic and magnetoelastic characterization and corrosion behaviour study (by potentiodynamic methods) of an Fe-based, Fe-Ni-Cr-Si-B metallic glass to be used as resonant platform for biological and chemical detection purposes. The same study has been performed in Fe-Co-Si-B (with excellent magnetoelastic properties) and Fe-Ni-B (with good corrosion properties due to the substitution of Co by Ni) composition amorphous alloys. The well-known, commercial metallic glass with high corrosion resistance Metglas 2826MB®($Fe_{40}Ni_{38}Mo_4B_{18}$), widely used for such biological and chemical detection purposes, has been also fully characterized and used as reference. For our Fe-Ni-Cr-Si-B alloy, we have measured values of magnetization (1.22 T), magnetostriction (11.5 ppm) and ΔE effect (6.8 %) values, as well as corrosion potential (-0.25 V), current density (2.54 A/m^2), and polarization resistance (56.22 $\Omega.cm^2$) that make this composition very promising for the desired biosensing applications. The obtained parameters from our exhaustive characterization are compared with the values obtained for the other different composition metallic glasses and discussed in terms of Ni and Cr content. https://doi.org/10.1063/1.4994108

I. INTRODUCTION

In the last years, the use of metallic glasses in the form of ribbons as magnetoelastic resonant platforms for sensing biological and/or chemical agents has received increased attention. Such devices performance allow remote "query and answer",[1,2] among others advantages as their low cost and low power consumption needed.[3] These magnetoelastic resonators are generally surface functionalized ribbon-shaped strips with different responsive recognition layers that provides diverse targets detection: aqueous chemicals including pH,[1] salt and glucose concentrations,[3] as well as inorganic salts deposition.[4] Also gas analytes as humidity,[5] carbon dioxide[6] and volatile organic compounds (VOCs) as benzene, hexane and others[7] can be detected. Recently, they have been successfully used as novel wireless biosensors for different pathogens as Salmonella,[8,9] Bacillus Anthracis spores[9] and Escherichia Coli.[10] Independently of gas, organic or inorganic target to be sensorized, in many cases such detection must be performed in water solution or aggressive media,

[a]Corresponding author: ariane.sagasti@bcmaterials.net

where arising corrosion produces a subsequent degradation of magnetic properties and sensing capacity.

Fe-rich, Fe-Co-Si-B metallic glasses show outstanding magnetic and magnetoelastic properties that increase the sensitivity to those detection processes, but they also show high tendency to corrosion. Figure 1 shows a clear example of this fact: in order to functionalize their surface, two equal length (3 cm) strips of commercial Metglas 2826MB®($Fe_{40}Ni_{38}Mo_4B_{18}$, high corrosion resistance), and a home-made metallic glass of composition $Fe_{64}Co_{17}Si_{6.6}B_{12.4}$ were immersed in a water solution containing an organic salt. After 4 hours, the corrosion effect is clearly visible for the homemade, Fe-rich ribbon.

Since the first Fe-based metallic glass was synthesized by liquid quenching in 1967,[11] rapidly quenched alloys became a new class of engineering materials for which the knowledge of their Glass Forming Ability (GFA) and corrosion resistance behaviour turn out to be fundamental aspects.[12] In particular, corrosion behaviour of these materials has been shown to be mainly controlled by the presence or absence of a protective, passive surface film that has to be stable not only in the medium where it was generated but also in other aggressive mediums. Thus, many studies already established that the use of Ni instead of Co[12] as well as the addition of Cr,[12–14] Zr, Mo and other elements greatly improve the corrosion resistance of metallic glasses at the expenses of some magnetic properties degrade. Nowadays, the same criteria apply to the fabrication and corrosion properties of bulk metallic glasses.[15,16]

Bearing all this in mind, in this work we report on the fabrication by melt spinning and the magnetic and magnetoelastic characterization and corrosion behaviour study (by electrochemical methods) of Fe based, $Fe_{64}Co_{17}Si_{6.6}B_{12.4}$, $Fe_{55}Ni_{25}B_{20}$ and $Fe_{54}Ni_{24}Cr_2Si_{10}B_{10}$ metallic glass ribbons. Values of magnetization, magnetostriction and ΔE effect, as well as corrosion potential, current density, and polarization resistance, are given and discussed in terms of Ni and Cr content. The well-known, commercial metallic glass with high corrosion resistance, Metglas 2826MB®($Fe_{40}Ni_{38}Mo_4B_{18}$), widely used for such biological and chemical detection purposes, has been also fully characterized and used as reference for the results obtained in our home-made metallic glasses.

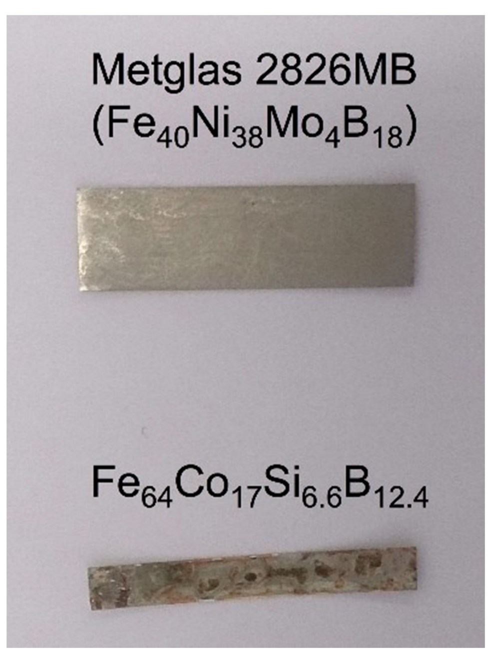

FIG. 1. Corrosion effect in commercial Metglas 2826MB and a homemade metallic glass of composition $Fe_{64}Co_{17}Si_{6.6}B_{12.4}$ (more details in the text).

II. RESULTS

A. Samples magnetic and magnetoelastic characterization

Figure 2 shows the hysteresis loops of the studied amorphous metallic alloys obtained with a VSM. The magnetic field was applied along the longitudinal direction of the ribbons, along the easy magnetization axis.

Figure 3 shows the magnetostriction measurements obtained for all the ribbons. The measurements were carried out including a passive gauge to compensate temperature drift effects. The ΔE effect was also measured for all the studied samples (see Figure 4).

Surprisingly, the alloy of composition $Fe_{55}Ni_{25}B_{20}$, even if we have measured its magnetostriction value to be of 16 ppm, shows almost no ΔE effect (below 1 %), a fact that tell us about the convenience of using this composition for other type of applications (like to be used in magnetoelectric laminates as magnetostrictive constituent, for example) better than applications based in mass load detection through magnetoelastic resonance frequency changes, where that resonance frequency has to be extremely sensitive to external parameters changes.

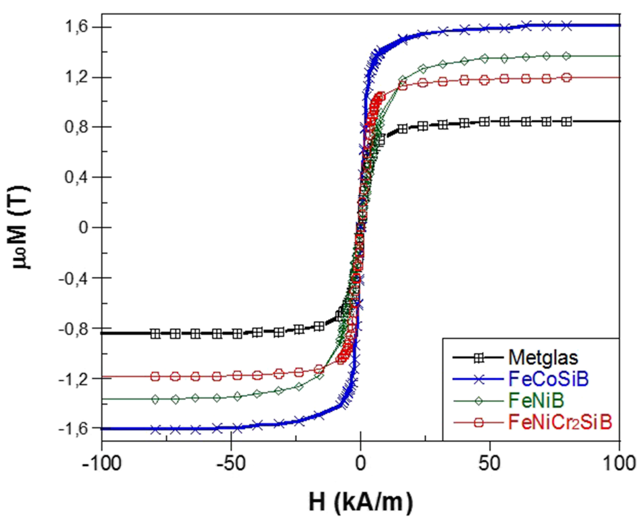

FIG. 2. Hysteresis loops measured for all the studied samples.

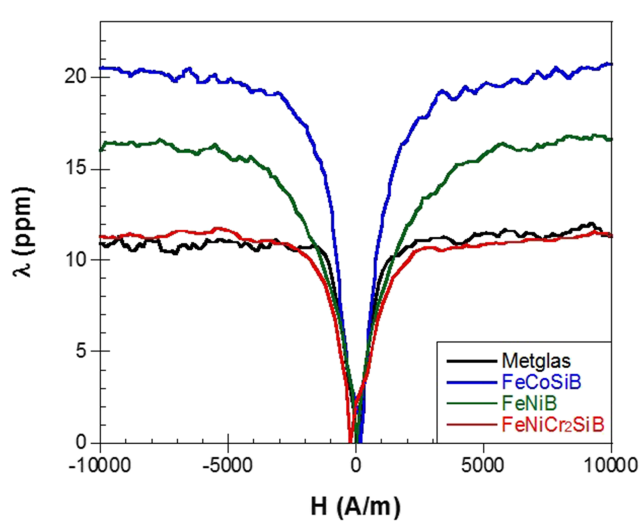

FIG. 3. Measured magnetostriction curves in equal strips of L = 3 cm, for all the studied samples.

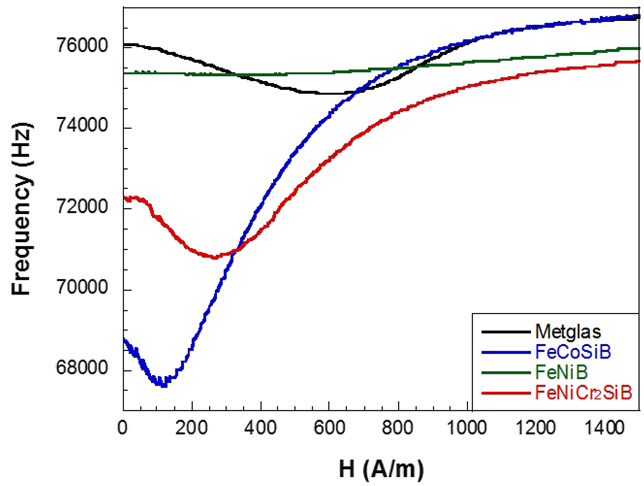

FIG. 4. Measured ΔE effect curves in equal strips of L = 3 cm, for all the studied samples.

TABLE I. Magnetic and magnetoelastic characterization of the ribbons.

Alloy	$\mu_0 Ms$ (T)	λ_s (ppm)	ΔE effect (%)
$Fe_{64}Co_{17}Si_{6.6}B_{12.4}$	1.65	20.5	13
Metglas 2826MB ($Fe_{40}Ni_{38}Mo_4B_{18}$)	0.88	11	2.5
$Fe_{55}Ni_{25}B_{20}$	1.41	16	0.9
$Fe_{54}Ni_{24}Cr_2Si_{10}B_{10}$	1.22	11.5	6.8

All the magnetic and magnetoelastic parameter values obtained from this characterization are summarized in Table I.

In which concerns the ability of these resonant platforms to be used for bio- or chemical sensing purposes, it is widely accepted that the basic equation that governs this magnetoelastic resonance-based detection process is:[17]

$$\frac{\Delta f}{f_0} = -\frac{1}{2}\frac{\Delta m}{m_0}, \tag{1}$$

where m_0 is the initially unloaded mass of the magnetoelastic platform that resonates at f_0, and $\Delta f = f - f_0$ is that resonant frequency change when a Δm uniformly deposited mass quantity attaches to the device. Such sensing platform is characterized by its mass sensitivity $S = -\Delta f/\Delta m = f_0/2m_0$ (Hz/g).[18] We can so make a first estimation about the good performance of our materials when working in such detection processes by making a quick magnetoelastic resonance measurement for equal strips of L = 1 cm length of each composition. Obtained frequency resonance values and corresponding detection sensitivities appear in Table II.

B. Electrochemical corrosion study

Linear Potential Resistance (LPR) measurements were carried out to determine the corrosion resistance of the different alloys and appear in Figure 5. These anodic polarization curves of the amorphous metallic alloys were performed in a three electrode conventional cell and were obtained

TABLE II. Estimated detection sensitivities for L = 1 cm equal strips of all the studied samples.

Alloy	m_0 (mg)	f_0 (kHz)	S (Hz/ng)	1/S (ng/Hz)
$Fe_{64}Co_{17}Si_{6.6}B_{12.4}$	2.11	222.750	0.053	19[18]
Metglas 2826MB ($Fe_{40}Ni_{38}Mo_4B_{18}$)	15.36	220.087	0.007	140
$Fe_{55}Ni_{25}B_{20}$	10.03	222.237	0.011	90
$Fe_{54}Ni_{24}Cr_2Si_{10}B_{10}$	4.32	218.150	0.025	40

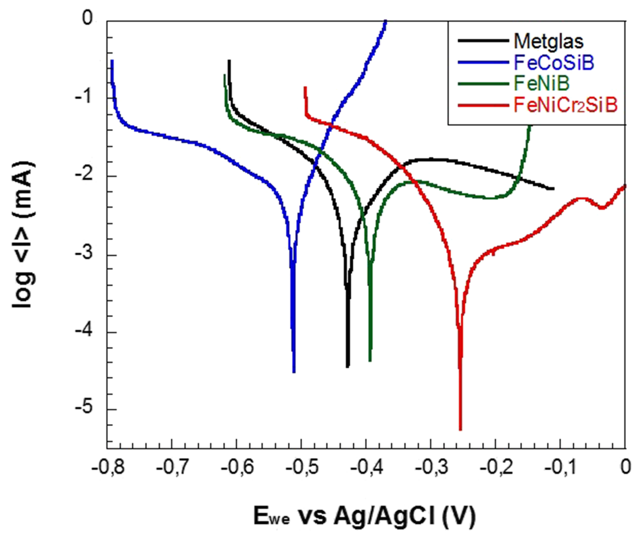

FIG. 5. Linear Potential Resistance curves for all the studied samples, measured in a PBS media at 25 °C and pH 7.3.

TABLE III. Results from the electrochemical corrosion study.

Alloy	E_{corr} (V)	j_{corr} 10^{-6} (A/cm^2)	R_p 10^3 (Ω cm^2)
$Fe_{64}Co_{17}Si_{6.6}B_{12.4}$	-0.51	8.18	11.74
Metglas 2826MB ($Fe_{40}Ni_{38}Mo_4B_{18}$)	-0.42	8.15	6.47
$Fe_{55}Ni_{25}B_{20}$	-0.39	13.07	7.41
$Fe_{54}Ni_{24}Cr_2Si_{10}B_{10}$	-0.25	2.54	56.22

in a PBS media of pH 7.3 at 25 °C with a scan rate of 0.5 mV/s. In Table III, all the data obtained from the LPR curves are summarized.

Cyclic Potentiodynamic Polarization (CPP) measurements were also performed, and obtained curves can be seen in Figure 6. From these curves, we can affirm that none of the studied samples show

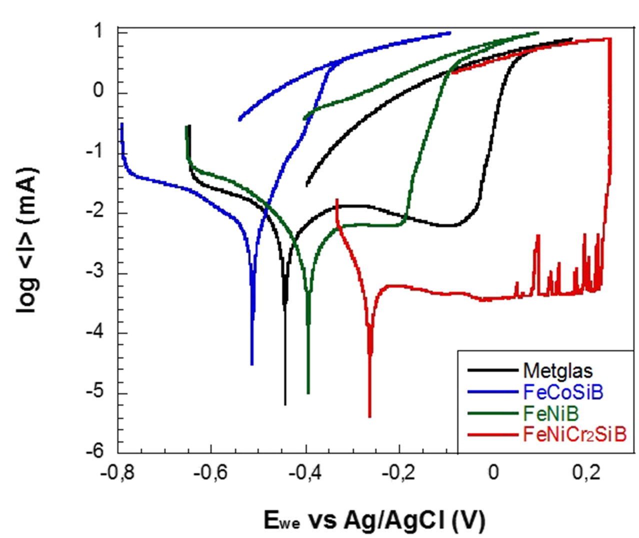

FIG. 6. Cyclic Potentiodynamic Polarization curves for all the studied samples, measured in a PBS media at 25 °C and pH 7.3.

any trend of passivation, except the Fe-Ni-Cr-Si-B composition alloy, that shows both a passivation region about 0.1 V and pitting corrosion from 0.2 V above.

III. DISCUSSION

As expected, our characterization of all the studied metallic glasses (home-made compositions and commercial Metglas 2826MB) show that the Fe-Co-Si-B composition shows the best magnetic and magnetoelastic performance and so it shows what in principle can be considered the best sensitivity when used for biological or chemical sensing applications with an estimated mass-to-frequency change sensitivity of 19 ng/Hz (see values appearing in Tables I, II and III). However, this composition shows the severe problem of corrosion, an important factor to be considered since usually all those detection processes happen with the magnetoelastic sample immersed in water or physiological solutions. Substitution of Co by Ni and adding a certain amount of Cr greatly improves the corrosion resistance behaviour of the alloys, as we have experimentally demonstrated. Nevertheless, the addition of Cr usually leads to a certain degradation of the magnetic and magnetoelastic properties of the fabricated alloy. In our case and for the Fe-Ni-Cr-Si-B fabricated composition, the fact that we have only introduced a 2 % at. of Cr makes this sample still to have good enough magnetic and magnetoelastic properties to be used as biological or chemical sensor, with an estimated mass-to-frequency change sensitivity of 40 ng/Hz, slightly higher than the corresponding value for the Fe-Co-Si-B resonator (due to the best magnetoelastic parameters of this last one), but still better than the values obtained for the Fe-Ni-B and Metglas 2826MB samples cases.

To confirm our previous assumptions on the corrosion resistance behaviour of our studied samples when containing Ni and/or Cr, an exhaustive electrochemical study has been performed. The characteristic electrochemical parameters obtained from the corrosion process are summarized in Table III. In these experiments, the corrosion potential (E_{corr}) value moves to more anodic (higher) values as the corrosion resistance of the sample increases. At the same time, the measured corrosion current (i_{corr}) shows a decrease, which makes the resistance parameter R_p to increase significantly. If we compare with the commercial Metglas 2826MB sample, our homemade Fe-Ni-Cr containing sample shows excellent magnetic, magnetoelastic and corrosion resistance properties to be used as resonant biosensing element.

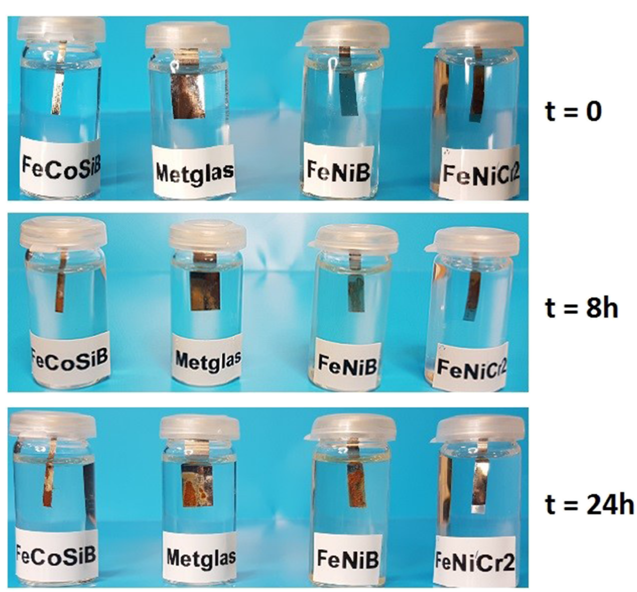

FIG. 7. Pictures taken a different times (initial time, after 8 hours and after 24 hours) for all the studied samples to visually observe the corrosion process.

As a visual proof of our observations, Figure 7 shows pictures taken at different times for the Fe-Co-Si-B, Fe-Ni-B and Fe-Ni-Cr-Si-B containing samples, in which the development of the corrosion process can be observed.

IV. MATERIALS AND METHODS

We have fabricated three different Fe based amorphous ferromagnetic alloys, with compositions $Fe_{64}Co_{17}Si_{6.6}B_{12.4}$, $Fe_{55}Ni_{25}B_{20}$ and $Fe_{54}Ni_{24}Cr_2Si_{10}B_{10}$ following the melt spinning technique. Samples were fabricated by using an Edmund Bühler GmbH© (Germany) Melt Spinner provided of a copper spinning wheel of 20 cm diameter. They were obtained in the form of long ribbons. The vacuum of the chamber was of about 10^{-5} mbar and the Ar overpressure to eject the melted alloy about 200 mbar. The distance between the crucible and the wheel was approximately 1.5mm and the speed of the wheel 44 m/s. For the different samples, diverse crucibles were used with different ejection hole diameters and therefore, the width of the fabricated ribbons varied for each composition. As reference for the corrosion behaviour study, we purchased also a commercial ribbon Metglas 2826MB of composition $Fe_{40}Ni_{38}Mo_4B_{18}$, with high corrosion resistance.

All studied compositions were fully magnetic and magnetoelastically characterized by measuring the corresponding hysteresis loops, magnetostriction and ΔE effect, all obtained values being summarized in Table I. Hysteresis loops were performed in a Vibrating Sample Magnetometer (VSM) MicroSens EZ7. Magnetostriction was measured by strain gauges KOYWA KFL-02-120-C1-11, using a Wheatstone bridge working in half bridge configuration including a passive gauge. Magnetoelastic measurements of the ΔE effect were carried out using the resonance-antiresonance technique and an experimental set-up consisting in three coaxial solenoids in order to apply the bias constant field (H), the alternating field to magnetostrictively excite the sample ($h.\cos\omega t$, $h<<H$), and a secondary pick-up coil to monitor the induced magnetization oscillations and detect the corresponding magnetoelastic resonance,[19] respectively.

The corrosion behaviour was studied by Linear Potential Resistance with a BioLogic VMP3 Potentiostat/Galvanostat. Measurements were made in a conventional cell with 3 electrodes; as working electrode (WE) we used our amorphous metallic alloys, as reference electrode (RE) an Ag/AgCl ingold electrode, and as a counter-electrode (CE) a platinum foil electrode. RE and CE were purchased from Methrom. We used as electrolyte a saline phosphate buffer solution 0.01M (PBS) purchased from Sigma (0.138 M NaCl and 0.0027 M KCl). The measurements were made at room temperature (25 °C) and at pH 7.3.[20]

Prior to measure the corrosion resistance behaviour, the samples were cleaned with acetone in sonication for 5 minutes and dried at room temperature to avoid any contamination form the fabrication or manipulation processes. To perform the measurements we left first the sample to stabilize for 30 minutes and measuring the open circuit voltage (OCV), and afterwards we force the working electrode to decrease -250 mV from the OCV and scan the potential in the anodic direction at 0.5 mV/s until 250 mV above that OCV. By analysing the obtained curves with the software EC-Lab (in particular Tafel fit and Rp fit) we obtained values for the corrosion potential (E_{corr}), the corrosion current density (i_{corr}) and the corrosion resistance (Rp), all obtained values being summarized in Table III.

V. CONCLUSIONS

The magnetic and magnetoelastic properties are affected by the composition of the amorphous metallic alloys. As expected, the addition of Cr decreases the saturation magnetization and magnetostriction. Nevertheless, a good ΔE effect has been measured for those samples showing a little dependence of the Young modulus with the applied magnetic field.

The polarization resistance experiments, made to study the corrosion behaviour of the different magnetoelastic amorphous alloys $Fe_{64}Co_{17}Si_{6.6}B_{12.4}$, $Fe_{45}Ni_{45}Mo_7B_3$ (commercial metglas 2826MB3), $Fe_{55}Ni_{25}B_{20}$, $Fe_{54}Ni_{24}Cr_2Si_{10}B_{10}$, have demonstrated that the alloy with the best behaviour against corrosion is $Fe_{54}Ni_{24}Cr_2Si_{10}B_{10}$ in a PBS media at 25 °C and a pH of 7. This sample has the highest corrosion potential, with the lower corrosion current density and a high polarization resistance. Besides, it has also a good ΔE effect, not as good as the other homemade alloys but the addition of chromium, which improves the corrosion resistance behaviour decreases the magnetoelastic properties of the material. Nevertheless, it is still better than the commercial alloy making this alloy also interesting for sensing applications.

The obtained results let us assume that we have improve the corrosion resistance of our homemade magnetoelastic material, not affecting too much the magnetostrictive properties which still make this alloys suitable for developing sensor with chemical or biological detection purposes.

ACKNOWLEDGMENTS

A. Sagasti wants to thank BCMaterials Centre for financial support. A. Sagasti and J. Gutiérrez would like to thank the financial support provided by the Basque Government under the MICRO4FAB (ELKARTEK program) and Research Groups IT711-13 projects. They would like also to thank Prof. A.R. Pierna from the UPV/EHU and Dr. J.M. Vega from Cidetec for very valuable conversations about corrosion in metallic glasses. A.C. Lopes thanks MSCA-IF-2015 (Marie Skłodowska Curie Actions) of the European Union's Horizon 2020 Programme for the received funds under grant agreement n° [701852].

[1] C. A. Grimes, W. R. Seitz, J. Horn, S. A. Doherty, and M. T. Rooney, "A remotely interrogatable magnetochemical pH sensor," IEEE Trans. Mag. **33**(5), 3412–3414 (1997).
[2] P. G. Stoyanov, S. A. Doherty, C. A. Grimes, and W. R. Seitz, "A remotely interrogatable sensor for chemical monitoring," IEEE Trans. Mag. **34**(4), 1315–1317 (1998).
[3] C. A. Grimes, C. S. Mungle, K. Zeng, M. K. Jain, W. R. Dreschel, M. Paulose, and G. K. Ong, "Wireless magnetoelastic resonance sensors: A critical review," Sensors **2**(7), 294–313 (2002).
[4] N. Bouropoulos, D. Kouzoudis, and C. A. Grimes, "The real-time, in situ monitoring of calcium oxalate and brushite precipitation using magnetoelastic sensors," Sens. Actuators B **109**, 227–232 (2005).
[5] C. A. Grimes, D. Kouzoudis, E. C. Dickey, D. Kiang, M. A. Anderson, R. Shahidain, M. Lindsey, and L. Green, "Magnetoelastic sensors in combination with nanometer-scale honeycombed thin film ceramic TiO_2 for remote query measurement of humidity," J. Appl. Phys. **87**(9), 5341–5343 (2000).
[6] Q. Y. Cai, A. Cammers-Goodwin, and C. A. Grimes, "A wireless, remote query magnetoelastic CO_2 sensor," J. Environ. Monit. **2**, 556–560 (2000).
[7] T. Baimpos, L. Gora, V. Nikolakis, and D. Kouzoudis, "Selective detection of hazardous VOCs using zeolite/Metglas composite sensors," Sens. Actuators A **186**, 21–31 (2012).
[8] R. S. Lakshmanan, R. Guntupalli, J. Hu, D. J. Kim, V. A. Petrenko, J. M. Barbaree, and A. B. Chin, "Phage immobilized magnetoelastic sensor for the detection of Salmonella typhimurium," Journal of Microbiological Methods **71**(1), 55–60 (2007).
[9] S. Huang, H. Yang, R. S. Lakshmanan, M. L. Johnson, J. Wan, I. H. Chen, H. C. Wikle III, V. A. Petrenko, J. M. Barbaree, and A. B. Chin, "Sequential detection of Salmonella typhimurium and Bacillus anthracis spores using magnetoelastic biosensors," Biosensors & Bioelectronics **24**(6), 1730–1816 (2009).
[10] C. Ruan, K. Zeng, O. K. Varghese, and C. A. Grimes, "Magnetoelastic immunosensors: Amplified mass immunosorbent assay for detection of Escherichia coli O157:H7," Anal. Chem. **75**(23), 6494–6498 (2003).
[11] P. Duwez and S. C. H. Lin, "Amorphous ferromagnetic phase in iron-carbon-phosphorus alloys," J. Appl. Phys. **38**, 4096 (1967).
[12] Y. Waseda and K. T. Aust, "Corrosion behaviour of metallic glasses," J. Mater. Sci. **16**, 2337–2359 (1981).
[13] R. B. Diegle, D. M. Lineman, and M. T. Thomas, "Repassivation kinetics of glassy alloys," Electrochem. Soc. Extended Abstr. **82**, 143 (1982).
[14] M. F. López, M. L. Escudero, E. Vida, and A. R. Pierna, "Corrosion behaviour of amorphous Fe-Cr-Ni-(Si, P) alloys," Electrochem. Acta **42**, 659–665 (1997).
[15] S. J. Pang, T. Zhang, K. Asami, and A. Inoue, "Bulk glassy Fe-Cr-Mo-C-B alloys with high corrosion resistance," Corrosion Science **44**, 1847–1856 (2002).
[16] M. Xu and Q. Wang, "Thermal stability and magnetic properties of Fe-Co-M-Zr-Nb-Ge-B (M = Mo, Cr) bulk metallic glasses," Progress in Natural Science: Materials International **24**, 116–120 (2014).
[17] P. G. Stoyanov and C. A. Grimes, "A remote query magnetostrictive viscosity sensor," Sens. Actuators A **80**, 8–14 (2000).
[18] A. Sagasti, J. Gutierrez, M. San Sebastián, and J. M. Barandiaran, "Magnetoelastic resonators for highly specific chemical and biological detection: A critical study," IEEE Trans. Mag. **53**(4), 4000604 (2017).
[19] J. Gutiérrez, A. Lasheras, P. Martins, N. Pereira, J. M. Barandiarán, and S. Lanceros-Méndez, "Metallic glass/PVDF magnetoelectric laminates for resonant sensors and actuators: A review," Sensors **17**, 1251 (2017).
[20] E. F. Marzo, A. R. Pierna, J. Barranco, G. Vara, A. Lorenzo, A. Pérez, and J. A. García, "Corrosion behaviour of Fe-Co based amorphous metallic alloys in saline solutions: New materials for GMI based biosensors," Portugaliae Electrochim. Acta **25**, 131–137 (2007), ISSN 0872–1904.