Novel Sensing Technique for Non-destructive Composites Monitoring

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Abstract— **In this paper, we observed the evolution of the transmission and reflection parameters of composites containing magnetic microwire inclusions during the composites matrix polymerization. A remarkable change of the reflection and transmission in the range of 4-7 GHz upon the matrix polymerization is observed. The observed dependencies are discussed considering variation of temperature and stresses during the thermoset matrix polymerization and their influence on magnetic properties of glass-coated microwires. The obtained results are considered as a base for a novel sensing technique allowing non-destructive and non-contact monitoring of the composites utilizing ferromagnetic glass-coated microwire inclusions with magnetic properties sensitive to tensile stress and temperature.**

Keywords- giant magnetoimpedance effect; magnetic microwires; magnetic softness; polymerization; composites.

I. Introduction

Amorphous magnetic materials can present an unusual combination of excellent magnetic properties (e.g., high magnetic permeability, Giant MagnetoImpedance (GMI), effect, magnetic bistability, Matteucci and Widemann effects) and superior mechanical properties (plasticity, flexibility) making them suitable for numerous industrial applications [1]-[6]. The aforementioned soft magnetic properties are originated by the absence of the magnetocrystalline anisotropy and defects (dislocations, grain boundaries, etc.), typical for crystalline magnets [1]-[3][6]-[8]. Furthermore, the preparation method involving rapid melt quenching is quite fast and inexpensive and the above mentioned magnetic softness can be realized without any complex post-processing treatments [3]-[5].

The development of novel applications of amorphous materials requires new functionalities, i.e., reduced dimensions, enhanced corrosion resistance or biocompatibility [8]. Therefore, great attention has been paid to the development of alternative fabrication methods allowing the preparation of amorphous materials at micro-nano scale involving melt quenching [6]-[8].

Glass-coated microwires prepared using the Taylor-Ulitovsky method fit to most of aforementioned expectation: such magnetic microwires have micro-nanometric diameters (typically 0.5-50 μm) covered by thin, insulating, biocompatible and flexible glass-coating [7]-[11] and can present excellent magnetic softness or magnetic bistability [7][9][11]. These features of the glass-coated microwires allow development of new exciting applications in various magnetic sensors [12]-[16], as well as in smart composites with tunable magnetic permittivity [17]-[19]. One more advantage of the glass-coated microwires is excellent mechanical properties [5].

Recently, the stress dependence of hysteresis loops and GMI effect are proposed for the mechanical stresses monitoring in Fiber Reinforced Composites (FRC) containing microwires inclusions or using magnetoelastic sensors based on stress dependence of various magnetic properties [18][20][21]. One of the common problems in the composite materials is the monitoring of the matrix polymerization as well as stresses monitoring. Usually, the polymerization process monitoring is performed by different sensors, like the pressure transducers and dielectric sensors [22]. However, employed sensors require direct contact with the resin and of its electronic associated [22]. One of the proposed solutions for non-destructive FRC monitoring is the use of piezoelectric fibers with diameters of 10 to 100 μm [23]. However, this solution requires electrical field supply plates occupying a significant area.

One of the promising solutions addressing the problem of non-destructive FRC monitoring is a novel sensing technique involving free space microwave spectroscopy utilizing ferromagnetic microwire inclusions presenting the high frequency impedance quite sensitive to tensile stress and magnetic field [17][18][24]. Mentioned above glass-coated microwires, with metallic nucleus diameters of 0.5 - 50 μm, presenting excellent mechanical and corrosive properties fit perfectly the requirements of this technique making it suitable for remote stresses and temperature monitoring in FRCs [17][18][24].

In this work, we provide our recent results on the study of stresses arising during the polymerization of the matrix in

FRCs on permittivity of the FRC with embedded microwire inclusions.

Consequently, in this paper, we present new experimental results on direct monitoring of the polymerization process in the FRC preparation using embedded Co-based glass-coated microwires.

In Section II, we present the description of the experimental techniques, while in Section III we describe the results on in-situ observation of the effect of matrix polymerization on the transmission, T, reflection, R, parameters of microwire arrays measured using the free-space system and compare them with the effect of applied tensile stresses on hysteresis loops of the studied microwires. We conclude in Section IV.

II. EXPERIMENTAL DETAILS

Glass-coated $Fe_{3.8}Co_{65.4}Ni_1B_{13.8}Si_{13}Mo_{1.35}C_{1.65}$ (metallic nucleus diameter, d=18.8 μm, total diameter, D=22.2 μm, ρ =d/D= 0.88) microwires with low negative magnetostriction coefficients, λ_s, have been prepared by Taylor-Ulitovsky technique described elsewhere [7][8][11][12]. As previously reported by us, as-prepared $Fe_{3.8}Co_{65.4}Ni_1B_{13.8}Si_{13}Mo_{1.35}C_{1.65}$ microwires present good magnetic softness, high GMI effect and low negative magnetostriction coefficients, λ_s, of about -0.1×10^{-6} [25][26].

The temperature during the polymerization process has been measured by a standard thermocouple.

For the composite matrix, we used a vinylester resin (DERAKANE 8084 resin), accelerated with Cobalt Octoate (0,3 pph) and catalyzed with Methyl Ethyl Ketona (MEK 60%, 1,5 pph). DERAKANE 8084 epoxy vinyl ester resin is an elastomer modified resin designed to offer increased adhesive strength, superior resistance to abrasion and severe mechanical stress, while providing greater toughness and elongation. The liquid resin exhibit the following properties: the density at 25°C is of 1.02 g/mL, the dynamic viscosity at 25°C is of 360 MPa and the styrene content is of 40%. All technical resin information appears in its technical data sheet (Document 1820 V5 F2, Language ES "draft", © 2017 Ashland Inc.).

Consequently, we used the free space measurement system, previously described in details in [18][24]. In this method, the microwire inclusions embedded in the polymeric matrix play the role of "the elementary scatterers", when the electromagnetic microwave irradiates the composite. At sufficiently high frequencies (GHz range), both the microwire magnetic and conductive properties will contribute to the microwave dielectric properties of the composite materials filled with short conductive microwire inclusions which now depends not only on the matrix and the embedded wires conductivity, but also on an effective ac permeability [18]. Consequently, the external stimuli (magnetic field, applied stresses, etc.) will significantly modulate the initial dielectric properties of the composite matrix [18].

In our free-space measurement system we followed the near field measurement scheme [18] which includes broadband horn antennas and the Through Reflection Line (TRL) free-space calibration. The reflection (*R*) and transmission (*T*) coefficients were measured in free-space. The experimental set-up consists of a pair of broadband horn antennas (1-17 GHz) and a vector network analyzer. The composite was placed in a 20 x 20 cm^2 window to avoid the edge effects. This window limits the applicable frequency range in 4-17 GHz. More detailed description of the free space systems is given in our previous publications [18] [24].

The composites with ordered glass coated amorphous wires embedded in the thermoset matrix polymerization were prepared (see Figure 1).

The polymerizing matrix provides external stimuli for the microwire inclusions (see Figure 1), which affects the magnetic properties and the GMI effect of microwires.

Hysteresis loops of single microwires have been measured using the fluxmetric method previously described

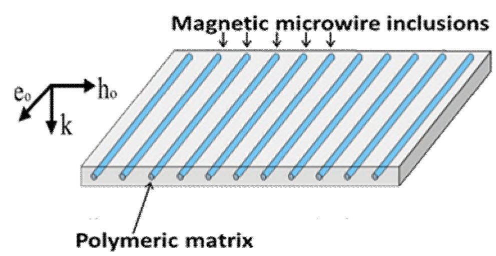

Figure 1. Sketch of a FRC with embedded microwires.

in details elsewhere [27]. In order to evaluate the influence of the external parameters (i.e., applied stress), similarly to that we recently described [22][28][29], we represent the hysteresis loops and normalized magnetization, M/M_0, versus magnetic field, H, where M is the magnetic moment at a given magnetic field and M_0 is the magnetic moment of the sample at the maximum magnetic field amplitude, H_m.

The stress has been applied during the annealing as well as during the sample cooling with the furnace.

Furthermore, the effect of applied stresses on hysteresis loops of individual microwires has been measured in order to compare with the effect of the matrix polymerization.

The value of applied stresses within the metallic nucleus has been evaluated as previously described [25]:

$$\sigma_m = \frac{K \cdot P}{K\ S_m + S_{gl}}, \tag{1}$$

where $k = E_2/E_1$, E_1 and E_2 are the Young's moduli at room temperature for the metallic alloy and the glass respectively, P is the applied mechanical load (up to 20 g), and S_m and S_{gl} are the cross sections of the metallic nucleus and the glass coating respectively. The value of the applied stresses evaluated using (1) was up to 472 MPa.

The Differential Scanning Calorimetry (DSC) measurements were performed using DSC 204 F1 Netzsch calorimeter in Ar atmosphere at a heating rate of 10 K/min up to temperature, T, of 900 ^{o}C.

However, the internal stresses, σ_i, arise during simultaneous rapid quenching of metallic nucleus surrounding by the glass coating due to the different thermal expansion coefficients. Consequently, the internal stresses magnitude can be controlled by the glass-coating thickness: the strength of internal stresses increases with the increasing of the glass-coating thickness [28]-[30][35].

III. EXPERIMENTAL RESULTS AND DISCUSSION

During the polymerization process of the resin, volume shrinkage of about 8.2 % occurs and solid cured resin is obtained. The mechanical properties of the cured resin are the following: tensile strength of 76 MPa, tensile modulus of 2,9 GPa, and tensile elongation of 8-10%. However, additionally to the matrix shrinkage a considerable heating takes place.

Therefore, in order to understand the processes during the polymerization of the composite that can affect the microwires, we have measured the evolution of temperature using a thermocouple. The obtained temperature changes during the polymerization represented at temperature, T, versus time, t, are shown in Figure 2. As can be observed from the Figure 2, the matrix polymerization produces a heating of the composite up to 80 ^{o}C.

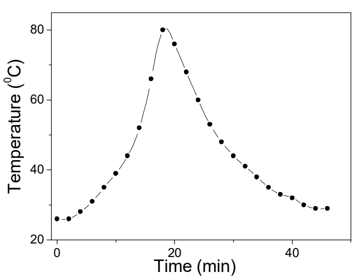

Figure 2. Evolution of temperature upon the polymerization.

In order to ensure that the employed microwires maintain their amorphous structure we performed the DSC studies of the crystallization temperature in order to evaluate the crystallization temperature. As can be observed from Figure 3 the crystallization temperature, T_{cr}, (determined as the beginning of the first crystallization peak) is about 554 ^{o}C (see Figure 3). Therefore, all the changes observed in the experiments must be attributed to the magnetoelastic behavior of the employed microwires only.

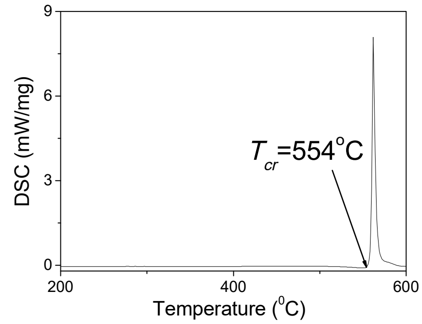

Figure 3. DSC curves of as-prepared $Fe_{3.8}Co_{65.4}Ni_{1}B_{13.8}Si_{13}Mo_{1.35}C_{1.65}$ microwires.

As described above, we performed in-situ experiments of composites placed inside the anechoic chamber with the glass-coated microwires embedded in a polymerized composite. We measured the transmission, T, and reflection, R, parameters of the composite containing Co-rich microwires ($Fe_{3.8}Co_{65.4}Ni_{1}B_{13.8}Si_{13}Mo_{1.35}C_{1.65}$) using the free space system.

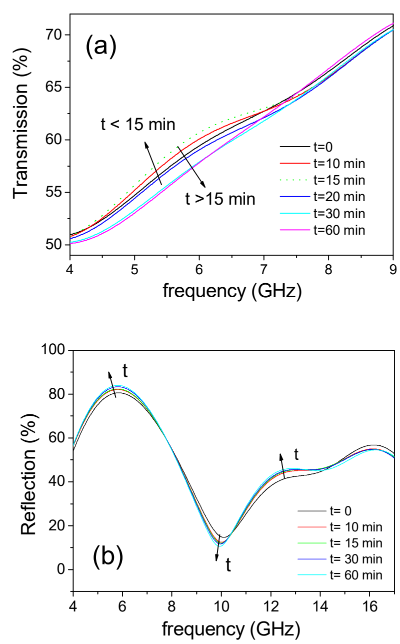

Figure 4. The Transmission, T (a) and reflection, R (a) parameters measured using the free-space system during the composite polymerization.

As can be appreciated from Figure 4, considerable variation of the T-parameter is observed in the range of frequency, f, of 4-7 GHz upon thermoset matrix polymerization (Figure 4). A non-monotonic variation of T-parameter upon polymerization is observed (Figure 4a). Additionally, some changes of R-parameter are also observed in a wide f- range (Figure 4b).

From experimentally measured T and R parameters, the absorption, A, parameter can be evaluated. Similarly to T

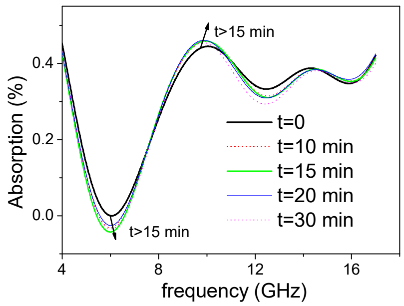

Figure 5. The Absorption, A, evaluated from data on T and R during the composite polymerization.

and R parameters, some changes in $A(f)$ dependence during the polymerization are observed (see Figure 5).

The observed changes of the electromagnetic properties can be related to two main phenomena arising during the composite matrix polymerization: heating and mechanical stresses.

As we mentioned above, the polymerization is accompanied by a change of density, matrix shrinkage heating. Although generally, the distribution of the internal stresses arising at polymerization is non-homogeneous [30], an important fact is that the matrix shrinks as it cools. Therefore, we can assume that the matrix shrinkage produces compressive stresses in the magnetic nucleus of the glass-coated microwires.

The observed $T(f)$ dependencies are non-monotonic: some increase of T observed up to t=15 min (at $f\approx$4-7 GPa)

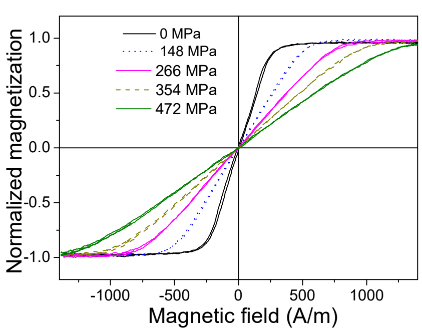

Figure 6. Effect of applied stress on hysteresis loops of as-prepared $Fe_{3.8}Co_{65.4}Ni_{1}B_{13.8}Si_{13}Mo_{1.35}C_{1.65}$ microwires.

followed by T decrease at t>15 min. Such evolution of T-parameter can therefore be associated with the heating and consequent cooling of the FRC.

However, the hysteresis loops of the studied samples are considerably affected by the applied tensile stresses, as shown in Figure 6.

To understand the effect of heating on the magnetic properties, we must consider the character of the internal mechanical stresses in the magnetic microwires. In fact, the main part of the mechanical stresses is originated by the difference in the thermal expansion coefficients of the metallic alloy and the glass-coating [31]-[34]. As shown elsewhere [35], the main part of the metallic nucleus of the microwire (up to $r \sim 0.85\ R$, where R is the metallic nucleus radius, r- metallic nucleus radius), has tensile stresses. Therefore, the difference in the thermal expansion coefficients of the metallic alloy and the glass-coating upon heating becomes smaller, allowing the reduction of the internal stresses. This assumption has recently been confirmed by direct observation of the heating effect on hysteresis loop of Co-rich microwires with vanishing magnetostriction coefficient [35]. The transformation of the hysteresis loop from linear to rectangular upon heating was explained by the easy anisotropy direction change from circumferential to axial upon heating.

In contrast to the temperature that non-monotonously changes during the polymerization, we assume that the compressive stresses, due to the matrix shrinkage, change monotonously. Therefore, we assume that the changes observed in Figures 5 and 6 are originated by both heating and matrix shrinkage during the polymerization.

Eventually, the same technique can be used for the remote monitoring of stress or temperature, not only during the polymerization, but also for real time non-destructive monitoring of local stresses and temperature during the exploitation of the composites.

IV. CONCLUSIONS

In this work, we propose a novel sensing technique for non-destructive and non-contact monitoring of the composites utilizing ferromagnetic glass-coated microwire inclusions with magnetic properties sensitive to tensile stress and temperature. To demonstrate it, we have studied in-situ the impact of the matrix polymerization on the evolution of the transmission and reflection parameters of the composites with microwire inclusions.

We observed a considerable variation of the T-parameter (in the range of 4-7 GHz) and R-parameter upon the composite polymerization using the free space technique. The observed dependencies are discussed considering the matrix shrinkage during the polymerization and heating during the matrix polymerization and their influence on the magnetic properties of the glass-coated microwires.

The obtained experimental results yield new and important insights suitable for the development of a novel sensing technique for non-destructive and non-contact monitoring of the FRCs utilizing ferromagnetic glass-coated microwire inclusions.

Consequently, a novel sensing technique for non-destructive and non-contact monitoring of the composites utilizing ferromagnetic glass-coated microwire inclusions with quite soft magnetic properties and tunable magnetic permittivity sensitive to tensile stress and temperature is proposed.

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