Monitoring the electrochemical behavior of hybrid coatings on magneto-elastic sensors using resonant frequency variations

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ABSTRACT

In this work we present results for the protective performance of coatings used on magneto-elastic ribbons. It is found that monitoring the resonance frequency variation (Δf) of a magneto-elastic sensor can give useful electrochemical information. This method has the advantage of allowing one to monitor the electrochemical behavior of coatings without the need for direct access to the sample. A sensor developed from the FeNiMoB alloy (Metglas 2826MB3) was covered with hybrid coatings based on silicon alkoxide precursors. The results obtained from the magneto-elastic sensor test were correlated with the results obtained from electrochemical impedance spectroscopy (EIS). In general, it was observed that the Δf monitoring technique provided results consistent with those obtained by EIS, with the advantage that it does not need to have direct contact with the sample. Besides that monitoring the resonance frequency also allows one to evaluate the electrochemical behavior of the coating in the medium of interest.

1. Introduction

One of the metal surface protection processes that has been extensively studied involves the development of hybrid coatings (organic-inorganic) based on silicon alkoxide precursors. The hybrid coatings combine the chemical, mechanical and thermal stability of the inorganic phase (ceramic) with the elastic and hydrophobic properties of the organic phase [1–9].

Among the main methods of evaluating the protective performance of coatings, electrochemical impedance spectroscopy (EIS) is the most used. In EIS analysis, the application of an alternating current allows one to analyze the behavior as a function of frequency. From the EIS analysis it is possible to study the general behavior of a system when several intercorrelated electrochemical processes occur at different speeds and/or corrosion rates [10–12]. In order to carry out this type of measurement, one normally uses a three-electrode cell with the sample immersed in the medium of interest and electrically connected to the devices necessary to carry out the measurement.

The use of a technique based on the measurement of the resonant frequency variation (Δf) of a magnetoelastic sensor coated with the coating, proposed in the present work, allows one to monitor the electrochemical behavior of the coating without the necessity of direct contact with the sample. Several authors have used magneto-elastic alloys in the study of specific properties of coatings, such as mechanical behavior [13], water absorption [14] and magnetic coupling [15]. In addition, several researches have been carried out with the use of this metal alloy as a biosensor platform for the detection of microorganisms [16–20].

It is known that when a ferromagnetic material is exposed to a variable magnetic field, its magnetic domains are oriented with this field, causing a variation in its dimensions. When the magnetic field is withdrawn, the magnetic domains may return to the disoriented configuration, leading to a return to the original dimensions of the material. Variations in the magnetization of the material result in a variation of the magnetic induction which is easily detectable [21–24].

Hybrid coatings deposited on the sensor will change its resonant frequency. The resonant frequency variation (Δf) is given in terms of the initial frequency of the sensor (f_0), the increase of the mass of the material (Δm) and the initial sensor mass (m_s), as shown in Eq. (1) [22–24]:

$$\Delta f = -f_0(\Delta m/2m_s) \tag{1}$$

In order to evaluate magneto-elastic materials with coatings for use in sensors, one can evaluate the properties and integrity of these coatings after periods of immersion in liquid media (electrolytes) of interest. Variations in the resonant frequency of the system (coated magneto-elastic material) are due to the mass increase.

This method can be indicated to evaluate the protective performance of various materials when applied on metallic surfaces. Examples include phosphatization, chromatization, organic coatings applied (resin, silane films, inks) [25–29]. In addition, due to its mass sensitivity, it can be used to evaluate moisture absorption in coating, as studied by Vebber et al. (2019).

Based on this, the objective of the present work is to evaluate the electrochemical behavior of hybrid coatings deposited on a Metglas 2826MB3 sensor by means of the Δf, correlating this measurements with those obtained by EIS.

2. Materials and methods

For this work, we used a substrate consisting of the magneto-elastic alloy Metglas®2826MB3, with average composition $Fe_{45}Ni_{45}Mo_7B_3$ (wt. %), purchased from the Metglas® Inc.. This material has a saturation magneto-striction of 12 ppm, a density of 7.9 g/cm^3, and an elastic modulus of 100–110 GPa. The alkoxide precursors used were 1.2-bis (triethoxysilyl)ethane (BTSE), tetraethoxysilane (TEOS) and 3-(trimethoxysilyl)propyl methacrylate (MAP), obtained from Sigma-Aldrich with a purity higher than 96%.

For the development of the magnetoelastic sensor, the Metglas ribbon was cut into strips with dimensions of 5 × 1 × 0.029 mm. The methodology used in the preparation of the substrate and in the development and application of coatings on the Metglas alloy was based on the work of Beltrami et al. (2017) [25].

For the EIS measurements, a conventional electrochemical cell was used with three-electrodes, a platinum wire being the counter electrode and a saturated calomel electrode (SCE) the reference electrode. The working electrode was the sample studied. The amplitude of the EIS signal was a sinusoidal 5 mV perturbation, and the frequency ranged from 100 kHz to 10 Hz with 10 points per frequency decade.

To measure the Δf, a variable magnetic field was produced by a Helmholtz coil giving rise to mechanical oscillations of the sensor with a characteristic resonant frequency. The permeation of the electrolyte through the coating or by the accumulation of corrosion products leads to an increase in the mass on the surface of the sensor and, consequently, a decrease of the resonant frequency, increasing the resonance frequency variation (Δf). This resonant frequency was measured, remotely and wirelessly, by a pick-up coil. For this measurement, an Agilent E5061B impedance analyzer was used, with a coupled pick-up coil at 23 °C. Resonant frequencies were measured continuously every 1 min for 24 h. This technique of analysis is number BR 10 2017 024116 5 patent deposit [30].

Both measurements were performed in triplicate on samples immersed in NaCl 0.05 M solution, with pH 8.4, conductivity of 10 mS. cm^{-1} and viscosity 1.0 cP. To evaluate the coating morphologies, we used a Tescan Mira3 field emission scanning electron microscope (FEG-SEM).

3. Results

Initially, the protective performance of the coatings was evaluated using the EIS technique, after 1 and 24 h of immersion in 0.05 M NaCl solution (Fig. 1). Subsequently, the Δf technique of the samples was monitored continuously during a 24 h period in 0.05 M NaCl (Fig. 2). Fig. 3 shows FEG-SEM images after 1 and 24 h of immersion in 0.05 M NaCl after the EIS and Δf measurements.

4. Discussion

From the results of the EIS measurement, it is observed that for both samples two different phenomena can be identified (Fig. 1.a). A phenomenon at high frequency (f > 10^2 Hz) and – phase angle of 35° for the TEOS-MAP sample and of 20° for the BTSE sample; another phenomenon is observed at low frequencies (f < 10^0 Hz) and – phase angle of 55°, for both samples. The high frequency phenomenon is associated with the presence of the protective coating on the metal surface [3,31,32]. The phenomenon at low frequency is related to the interfacial processes between the coating and the electrolyte, such as permeation, diffusion and transfer of charge [33,34].

After 24 h of immersion in 0.05 M NaCl solution (Fig. 1.a), it is seen that the TEOS-MAP sample showed the same phenomena observed after 1 h of immersion. However, the value of the – phase angle is reduced to 25° at high frequency. This behavior indicates that the protective effect of the film is still active, however, due to its permeability, this effect was reduced with increasing immersion time.

For the BTSE sample after 24 h of immersion in NaCl 0.05 M (Fig. 1. a), no phenomena are observed at high frequency. However, we observed two phenomena coupled at medium and low frequencies (10^{-1} < f < 10^2 Hz) with – phase angle around 50°, indicating the high permeability of this film. This result is confirmed by the decrease in the impedance modulus log (Fig. 1.b) at low frequencies for the BTSE sample.

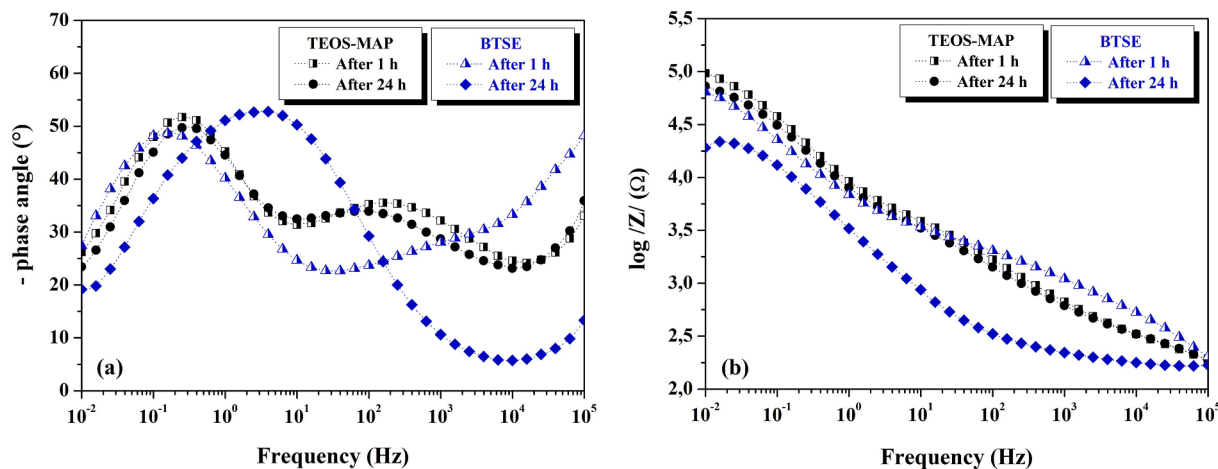For a continuous evaluation of the protective performance of the

Fig. 1. Bode diagrams correlating (a) phase angle with frequency and (b) impedance modulus log with frequency, obtained from EIS measurements for the samples studied during 1 h and 24 h in 0.05 M NaCl solution.
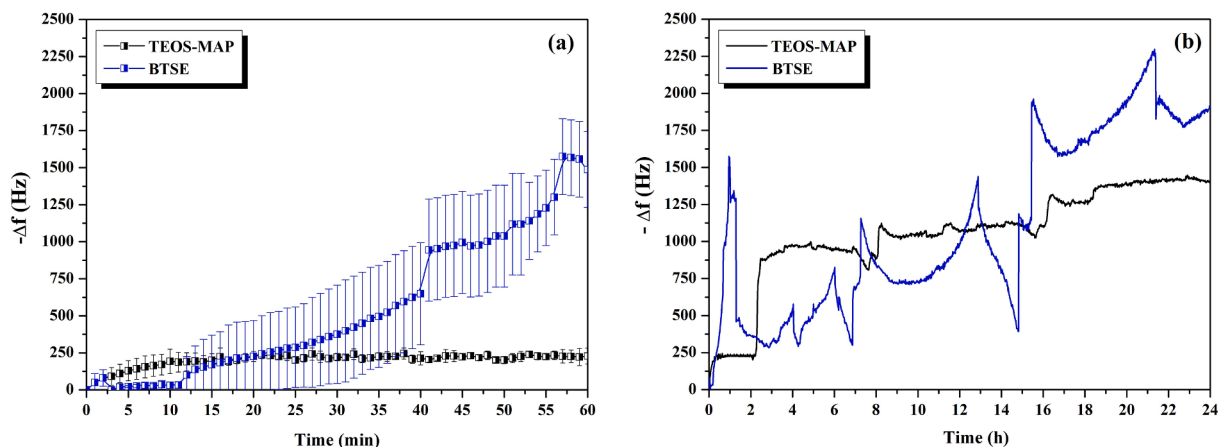
Fig. 2. Measurements of1 Δf for the samples studied in 0.05 M NaCl solution during (a) 1 h and (b) 24 h.
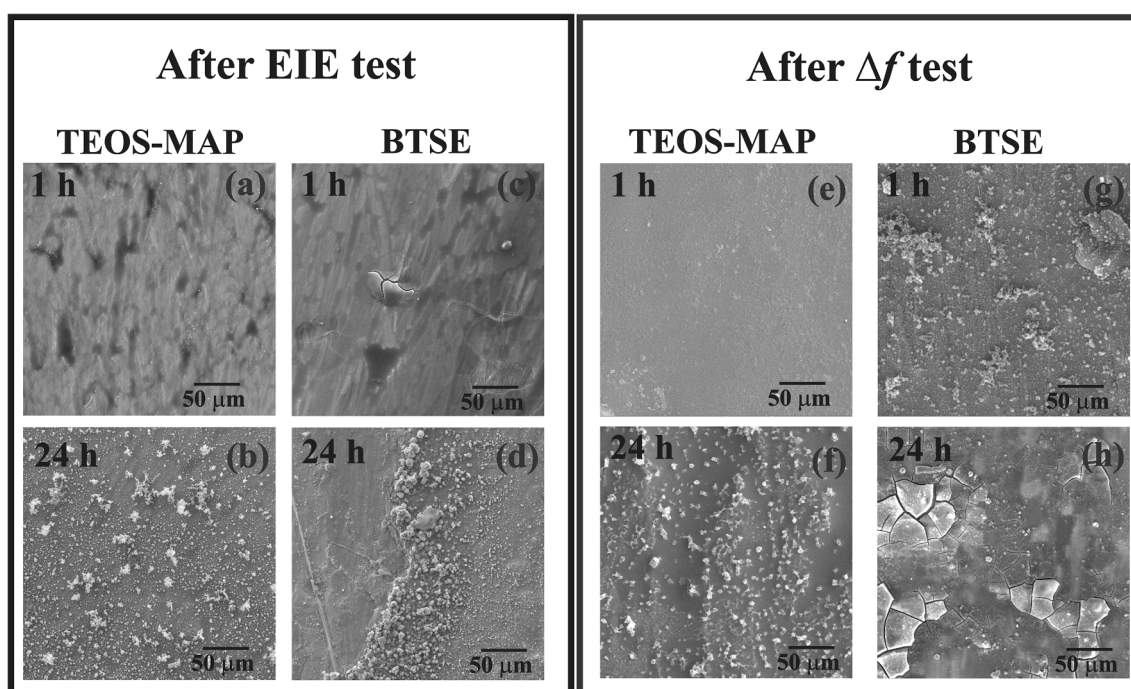

Fig. 3. FEG-SEM images after 1 h (a, c, e, g) and 24 h (b, d, f, g) in 0.05 M NaCl solution during the EIS and Δf measurements.

coatings, the resonant frequency of the coated magnetoelastic sensor was monitored. The Δf measurements allowed us to continuously follow the evolution of the electrochemical behavior of the coatings immersed in the medium of interest without direct contact with the sample, accurately highlighting the events and changes in the coating throughout the test period.

For the TEOS-MAP sample, a frequency shift Δf of around 200 Hz was observed, which remained stable for 60 min of immersion in NaCl 0.05 M (Fig. 2.a). This variation is related to the stabilization of the sensor in the liquid medium, since the density and the viscosity of the medium directly affect Δf, generating a damping of the oscillations of the sensor. Wen et al. [35] point out that, depending on the analyzing medium to which the magneto-elastic sensor is exposed, damping forces affect the surface. These damping forces reduce the resonant frequency of the magnetoelastic sensor because they prevent vibrational oscillations, changing the behavior [35].

The stable behavior of the TEOS-MAP coating over 60 min of immersion in NaCl 0.05 M is associated with its good electrochemical performance, indicating that it is resistant to electrolyte permeation.

This result is in agreement with the one observed in the EIS measurement (Fig. 1.a), where the TEOS-MAP sample presented high frequency phenomena associated with the protective character of the coating. In both tests, no corrosion products were formed on the surface of the samples after 1 h, as observed in the FEG-SEM (Fig. 3a and e) micrographs, confirming the inferences discussed above.

After 2 h of immersion (Fig. 2.b), it is observed that the TEOS-MAP sample shows an increase in Δf, which evolves incrementally over the 24-hour monitoring, with jumps around 8 h and, later, around 16 and 18 h. This behavior is possibly associated with permeation of the electrolyte through the coating and the beginning of the corrosion process, which invariably reaches the substrate and promotes the formation of oxides.

The formation of oxides leads to an increase of the mass on the sample and a decrease in frequency. This behavior agrees with the results observed by EIS (Fig. 1.b), where the TEOS-MAP coating showed a decrease in its protective action after 24 h of testing. This is also confirmed by FEG-SEM micrographs, where corrosion products were observed on the surface of the samples in both tests after 24 h of

immersion (Fig. 3.b and .f).

The BTSE sample presented a sharply decreased frequency in the first instants of immersion in NaCl 0.05 M (Fig. 2.a). This result can be associated to the interfacial reactions between the coating and the electrolyte and also to the permeability of the film, which allows the absorption of electrolyte, thus promoting the increase of mass on the sensor and, consequently, a decreased frequency.

The result corresponds to that observed by EIS (Fig. 1a), where the BTSE coating presented a very discrete phenomenon at high frequency, indicating a weak protective action. These results are corroborated by the FEG-SEM (Fig. 3.c and .g), where it is possible to observe that, after 1 h of testing, the coating shows cracks, displacement and corrosion products, attesting to its poor electrochemical performance.

As the immersion time increases (Fig. 2.b), frequency measurements indicate that the BTSE sample presented several mass gain and loss events. These oscillations of Δf may be related to the electrolyte absorption by the coating, indicating the presence of discontinuities; or the presence of corrosion product (formation, release and solubilization) resulting from the action of the electrolyte directly on the metal. This behavior indicates inefficient protection by this coating.

From the increasing evolution of the frequency (Fig. 2.b), after 14 h of testing, an expressive event is observed, implying a constant decline in the protective effect of the BTSE coating. In the EIS test, this is evident after 24 h of immersion, where only low frequency events are observed, associated with the formation of oxides and corrosion products (Fig. 2.b). From the images obtained by FEG-SEM after 24 h of immersion (Fig. 3.d and .h) it is possible to observe the presence of corrosion products formed on the surface of the sample coated with BTSE, both for the samples evaluated by EIS and for those evaluated by frequency measurements, which confirms the poor electrochemical performance of this coating.

In general, it can be observed that the frequency monitoring technique provided results consistent with those obtained by EIS, with the advantage that it does not need to have direct contact with the sample and also allows instantaneous evaluation of the behavior of the coating of interest.

5. Conclusions

From the monitoring of the resonant frequency variation of the magnetoelastic sensor it was possible to monitor and record constantly and instantaneously, during the entire test period, the evolution of the events on the surface of the sensor.

The results obtained from frequency measurements were coherent with those obtained by EIS. In both techniques, the results indicated the poor electrochemical performance of the BTSE coating when compared to the TEOS-MAP coating. The results also showed that the TEOS-MAP coating more efficiently protected the substrate when immersed in 0.05 M NaCl solution. This result was supported by the events at high and medium frequencies observed by EIS and the minimal variation of the resonance frequency.

In summary, it is concluded that the resonant frequency measurements can be considered as an efficient technique to control the electrochemical performance of the coatings tested. It is also emphasized that all the monitoring of the coatings can be performed without the need of electrical contact with the samples (without direct connections).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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