New Structure for Corrosion Evolution Detection

Jamal Rammal[1], Farah Salameh[1], Wassim Rammal[2], Jamil Fouany[1], Hassan Mehdi[1],Yaakoub Dia[1]

[1] *Technology department, MUC University, Lebanon.*
[2] *Faculty of Sciences, Lebanese University, Lebanon.*
* *jrammal@muc.edu.lb*

Abstract. This article presents a microwave sensor capable of detecting and following the evolution of the corrosion of zinc material. This sensor is based on zinc wires of different widths deposited on the surface of the ceramic resonator. Numerical studies show that due to the evolution of the corrosion, the progressive degradation of the conductivity of the formed zinc grid (from 6S/µm to 0.015S/µm) cause a progressive frequency shift (230MHz), a degradation of the quality factor (from Q0 = 50 to Q0 < 5) and a decreased level of the coefficient transmission of the TE101 mode of the resonator (from -8dB to <-35dB). Experimental measurements of this sensor in a corrosive environment show a gradual shift of the resonance frequency of the TE101 mode, a decreased level of S21 transmission coefficient and a degradation of the unloaded quality factor.

Keywords: Corrosion, ceramic, detection, evolution, conductivity, degradation.

1. Introduction

Most metals are thermodynamically unstable in atmospheric conditions. In order to maintain the metal form, metals must absorb and store energy [1]. Some metals require a high energy, such as aluminium or magnesium, while others require a lower energy such as gold [2]. If this needed energy is not supplied, the metal will revert to a lower energy state. This transition from a metal to a metal oxide exemplifies corrosion. The main effects of corrosion on metal can be presented by a combination of several factors: Progressive degradation of conductivity and progressive presence of insulating zones.

Corrosion is one of the major damage mechanisms affecting different structures, including bridges, pipelines, and transportation structures such as marine ships and aircrafts that normally operate in a corrosive environment.

Economically, the corrosion consequences are of high importance. Replacing corroded equipment and materials is a very high financial charge for the industry.

The corrosion detection in the early stages is very important to ensure the safety of these structures and, therefore, of their users. For this aspect it is interesting to monitor, continuously, the corrosion state in structures that operate in a corrosive environment.

There are several traditional techniques for the corrosion detection and monitoring. The visual technique [3], the radiographic technique [4], Luna sensor [5]. The main disadvantages of these techniques are, the surface to be inspected should be clean, accessible, high cost of equipment, uses of active components (power supply needs to be integrated in the sensor).

However, since corrosion is a very long process (several years), the sensor must have a long-term life and this is very restrictive for active sensors when they are integrated into the structure potentially inaccessible. The limitations of traditional techniques show the need for a corrosion sensor that must be economic, sensitive, and passive.

The publications in this field are very limited. In 2011, Pasupathy et al. [6] have proposed a totally passive sensor for monitoring corrosion of steel in reinforced concrete. The sensor operates at 2.5 MHz. From an economic point of view, the manufacturing cost of the sensor is low. However, the sensor does not give information on the level of corrosion, and there is a transition between the two modes (not corroded, corroded). Therefore, the user does not know the start of corrosion. Kenneth Loh et al. [7] presented a corrosion sensor based on a thin film of carbon nano tube. The corrosion-induce change a property of the thin film of carbon nano tube, and this change causes a frequency change of the resonant circuit. The sensor operates at 2MHz. The main disadvantage of this sensor is its high manufacturing cost.

In this paper, we propose a microwave passive sensor that allows us monitoring the evolution of the zinc corrosion, the zinc is selected for its wide use in the transportation industries (marine ships and aircrafts). We present electromagnetic studies on Alumina resonator. Studies include the electromagnetic response change of structure affected by the different effects of corrosion. These studies allow us to understand and predict the behaviour of the sensor when exposed to a corrosive environment. Then we describe the various experimental measurements to validate the theoretical results.

2. General description of the structure

The designed structure is shown in Figure 1. It consists of Alumina substrate, 25mm * 25mm with a thickness 1mm, the substrate faces are covered with a copper layer of 3µm protected against corrosion by a 200 nm layer of gold (yellow area) except for the center of the top face where a 3µm of a zinc layer (gray area) of conductivity 6 S/µm and of thickness 3µm divided into wires of widths 200µm, 400µm and 600µm is deposited (the theoretical conductivity of the zinc is 16 S/µm but different experimental measurements of the zinc conductivity in the laboratory give a value around 6S/µm). Zinc wires can be considered as the sensitive area of our sensor.

To avoid an electrochemical cell between zinc wires that

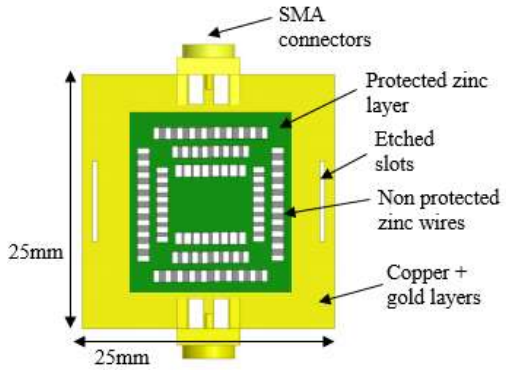


Fig. 1. Sensor design: TE_{101} Alumina resonator

are sensitive to corrosion and the copper protected from corrosion by gold (two metals of different natures), a zinc area that is not sensitive to corrosion (green zone) is deposited around the wires (this area will be protected by a resin AZ4533 once the sensor is formed).

The resonator excitations are done by 50Ω short circuited coplanar lines that are compatible with SMA connectors. Using this type of connectors is preferred due to their compatibility with the wiring system used in the sensor measurements in special enclosures such as those used in corrosion testing chambers. Both patterns in the form of slots on both ends of the sensor are optimized to adjust the resonant frequency of the TE_{101} mode at 2.45 GHz (ISM band) of the ceramic substrate.

The distribution of the zinc wires are optimized so that the sensor is able to follow the evolution of zinc corrosion. Alumina (Al_2O_3) is chosen due to it higher resistivity against corrosion compared to organic materials, and this is due to the low solubility of chemical components of ceramics and its good chemical stability [8], [9], we did not take into account the temperature coefficient of permittivity into account. In addition, Al_2O_3 has a low loss tangent (in the order of 10^{-4}), which increases the quality factor of the resonator and hence the sensor sensitivity. In terms of compactness, the alumina has a good mechanical strength and hardness and good resistance against erosion [10]. Finally, this material is relatively less expensive than some of currently used compounds.

The sensor transmission coefficient S_{21} in dB is shown in Figure 2 (dotted line). The resonance frequency of TE_{101} mode is 2.45GHz, the unloaded quality factor Q_0 is 55 and the level of S_{21} is -7.5dB, In future work the sensor will be investigated by an antenna, for this reason we selected this level of coupling.

Numerical simulations on Ansoft / HFSS were performed on the designed sensor in order to study the variation of the electromagnetic response of the sensor once it is affected by the degradation of conductivity of metals deposited on their surface.

The conductivity of the metallization covering the resonator is fixed at 45S/µm and the zinc wires conductivity varies from 6S/µm to 0.015S/µm. The lack of conductivity values in the 2.45 GHz region of corroded metals led us to conduct studies with different conductivity values.

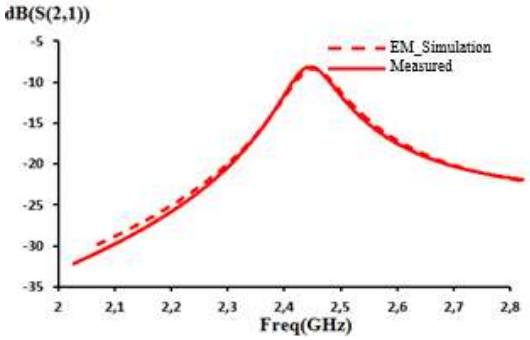


Fig. 2. Measured and simulated results of transmission coefficient S_{21}(dB) of non-corroded sensor

The choice of these values is based on the results presented by E. Diler et al [11] who shows that the conductivity of the corroded metal decreases gradually with metal loss due to the gradual creation of relatively insulating corrosion products. Hence, the chosen conductivity value can range from the conductivity value of the non-corroded metal to a zero conductivity which presents a perfect insulating medium.

Figure 3 shows the transmission coefficient S_{21} in dB of the resonator for the conductivity values ranging from 6S/µm to 0.015S/µm (dotted curves). The level of S_{21} and the unloaded quality factor of the TE_{101} mode decreases progressively with the gradual decrease in the conductivity of zinc wires, and for a conductivity of 0.015S/µm, the unloaded quality factor of TE_{101} mode is < 5 and the level of S_{21} is < -35dB. For lower conductivity values, we have a total loss of the resonance peak. Regarding the resonant frequency of the TE_{101} mode, the frequency begins to shift significantly towards lower frequencies (ΔF>10MHz) starting from a conductivity of 0.12S/µm of the zinc wires.

This frequency continues to gradually shift toward the low frequencies, and for a conductivity value of 0.015S/µm, the frequency offset is ΔF = 230MHz. For lower conductivity values, we have a total loss of the resonance peak.

The gradual decrease in the level of S_{21} and the unloaded quality factor and the frequency shift are explained by the increase of the resistivity of zinc wires. This effect can be modeled by creating resistors on the surface of the resonator in the locations of wires. The value of this resistance increases with the decreasing conductivity, which leads to the gradual decrease in the level of S_{21} and the unloaded quality factor and the frequency shift.

In conclusion, if the corrosion causes a gradual decrease in the conductivity of zinc wires (to a value of 0.015S/µm), the developed sensor allows us to monitor corrosion of zinc by monitoring the resonant frequency, the quality factor and the level of S_{21}.

3. Sensor fabrication

A substrate of alumina 25mm*25mm of 1mm thickness was metallized with a copper layer of 3 microns by Electroless 3D. Then a layer of 200 nm of gold is deposited on the copper metallization by electrolysis to protect the copper from oxidation (Figure 4.a). A standard lithography

process is used to etch the surface in order to pattern the coplanar access, the slots and the position of the zinc layer. Metallization of 5mm was carried out on the walls at the SMA level to avoid short circuits.

After this process, a protection layer of resin is placed around the central etched zone (Figure 4.b). A zinc layer of 3µm is deposited in the etched area at the center of the sensor by cathode sputtering (PVD). After the deposition of zinc by PVD, the sensor is then rinsed with acetone to remove the zinc deposited on the resin and keep the zinc deposited at the center of the sensor (Figure 4.c).

The last two stages of implementation are the etching of zinc wires and the protection of areas surrounding these wires by AZ4533 resin (we recall that we protect these areas to avoid having an electrochemical cell). These two steps are carried out by lithography. Figure 5 shows the final sensor after etching zinc wires, the protection of areas surrounding these wires and the welding of SMA connectors.

4. Experimental measurements

First we measured the transmission coefficient S_{21} in dB of the sensor with a network analyser Rohde & Schwarz, ZVL (9KHz 13.6GHz).

The resonant frequency of the TE_{101} mode is 2.45GHz, the unloaded quality factor Q_0 is 50, and the level of S_{21} is -8dB. The figure 2 (dotted and solid lines) show a comparison between the measured and simulated responses of the sensor. The experimental results are in good agreement with the theoretical results.

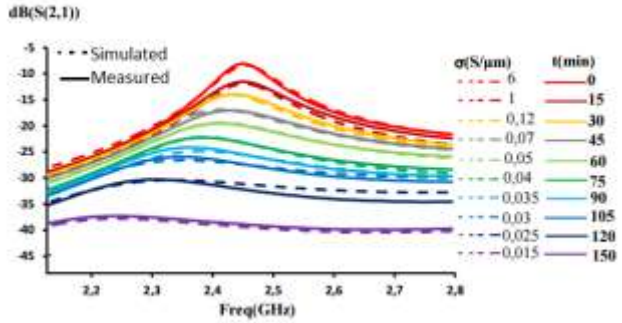


Fig. 3. Transmission coefficient S_{21}(dB) simulated and measured for corroded sensor

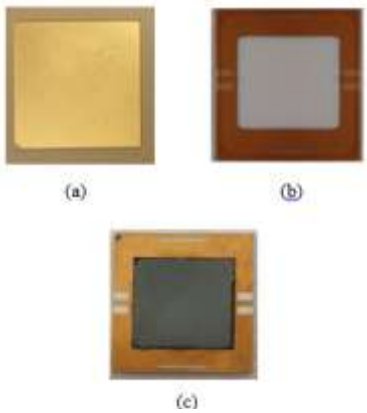


Fig. 4. (a) Metallized Alumina substrate, (b) etching the gold and the copper layer, (c) deposition of zinc by PVD

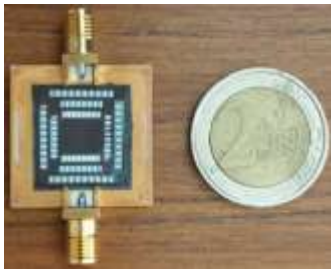


Fig. 5. Final sensor

4.1. Measurement of the sensor in a corrosive medium

The use of chamber for salt spray test, or the use of humidity test chambers that produces an atmosphere conducive to corrosion that attacks the piece under test is the best place to test our sensor.

For this purpose we have prepared an enclosure which contains a K_2SO_4 potassium sulfate solution. This solution generates a reference humidity of 97% in the enclosure [11]. Before placing the sensor in the enclosure, and as zinc corrosion in a moist environment is a long process that can take several months, it is important to introduce a saline solution on the zinc in order to accelerate its corrosion. This allows us to observe the behavior of the sensor in a few hours instead of waiting several months. For this purpose we introduced a methanol solution containing sodium chloride (3.3g / l). This method of salt deposit has been already used by E.Diler et al. [11] and Prosek et al. [12] with success.
After the deposit of the saline solution, the sensor was dried and fixed in the upper side of the enclosure without contact with the K_2SO_4 solution as shown in Figure 6. Every 15 minutes an acquisition by the VNA of the transmission coefficient S_{21} in dB has been achieved.

Figure 3 (solid line) shows the variation of the transmission coefficient S_{21} in dB of the sensor over time. The level of S_{21} and the unloaded quality factor TE_{101} mode gradually decrease with time. At t = 0, the level of S_{21} = -8dB and Q_0 = 50. The level of S_{21} and the quality factor decrease gradually with time, and after t = 150mins, the level of S_{21} decreases by -29dB (S_{21} = - 37.2dB) and the quality factor by 92% (Q_0 = 2). After t = 180mins we lose completely the resonance peak of the TE_{101} mode. Regarding the resonance frequency of the TE_{101} mode, it remains stable in the first 15 minutes, and after 30 minutes it starts to shift toward the low frequencies in a remarkable manner (ΔF = 13MHz).

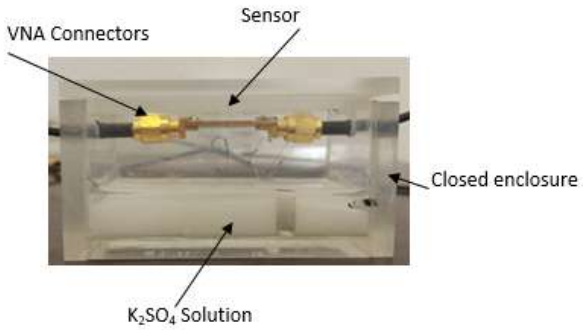


Fig. 6. Enclosure which contains the sensor and K_2SO_4 solution

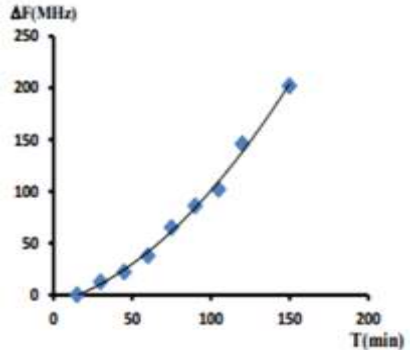
This frequency continues to shift progressively towards lower frequencies with time and at t = 150mins, it shifts by 230MHz (F = 2.22GHz). After 180mins we lose completely the resonance peak of this mode.

Figure 7.a, b, c, d, summarizes the variation of the frequency shift of the TE_{101} mode with respect to the initial frequency over time, the variation in the level of the transmission coefficient S_{21} in dB of the TE_{101} mode with respect to the initial S_{21} over time, the variation of the quality factor of TE_{101} mode over time, the variation in the level of the transmission coefficient of the TE_{101} mode as a function of the frequency shift of this mode and the variation of the quality factor the TE_{101} as a function of the frequency shift of this mode, respectively.

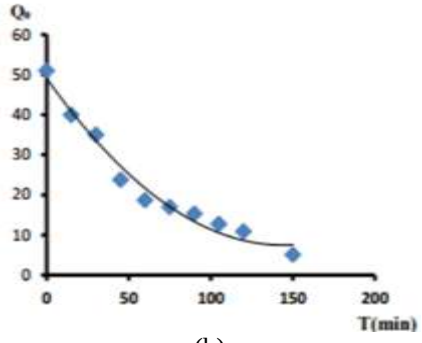
Comparing with the electromagnetic simulations, the sensor response is consistent with our expectations. We have a progressive shift of the resonance frequency of the TE_{101} mode (from 2.45GHz to 2.22GHz), a decrease in the level of the transmission coefficient S_{21} (from -8dB to -37dB) and a degradation of the unloaded quality factor Q_0 (from 50 to 4). These variations are due to the evolution of the corrosion of zinc wires with time.

5. Conclusion

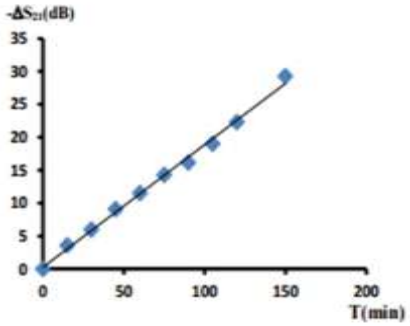
In conclusion, we have presented a microwave sensor capable of detecting and tracking the evolution of zinc corrosion. The detection of corrosion is based on the variation of the physical properties of zinc wires distributed on the sensor surface once corroded. Numerical studies show that the progressive degradation of the conductivity of the zinc grid (from 6S / µm to 0.015S/µm) causes a high decrease in the level of the transmission coefficient of the TE_{101} mode, a high degradation of the unloaded quality factor and a frequency shift to lower frequencies.



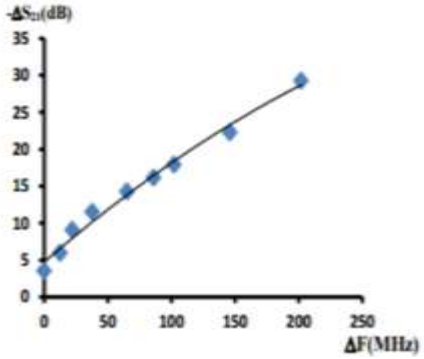
(a)



(b)



(c)



(d)

Fig. 7. (a), (b), (c), (d), variation of the response of the sensor over time

These results show that using this sensor, regardless of the effect of corrosion on zinc wires, we are able to follow the evolution of the zinc corrosion. Experimental measurements of the sensor in a corrosive environment show a gradual shift of the resonance frequency of the TE_{101} mode (from 2.45GHz to 2.22GHz), a decrease in the level of the transmission coefficient S_{21} (from -8dB to -37dB) and a degradation of the unloaded quality factor (from 50 to 4). These variations are due to the evolution of the corrosion of zinc wires with time. Microscopic studies show that the corrosion of zinc wires leads to the creation of corrosion products.

Based on these results, we can explain the frequency shift of the TE_{101} mode sensor, the degradation of the quality factor of this mode and the decrease of transmission coefficient level by the progressive presence of corrosion products, which causes the gradual decrease of the overall conductivity of each zinc wires on the top of the sensor.

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Biography of the authors

Jamal Rammal: He received the Ph.D in circuits, systems, and micro and nanotechnology for optical and high-frequency communications from XLIM Laboratory, Limoges, France in 2014. His research interests include microwave characterization of dielectric materials, microwave sensors and microwave processing.

Farah Salameh got her MSc and her PhD in electrical engineering from the National Polytechnic Institute of Toulouse (INPT), Toulouse, France, respectively in 2013 and 2016. Her main research interest is the development of statistical methods for the modeling and the validation of electrical engineering component lifespan.

Wassim M. Rammal was born in Lebanon, in 1977. He received the Ph.D in Physics and Optoelectronics from XLIM Laboratory, Limoges, France in 2006. He is currently an Assistant Professor at Lebanese University, Faculty of Sciences, Lebanon. His research interests include photovoltaic system.

Jamil Fouany was born in Lebanon, in 1989. He received the Ph.D in circuits, systems, and micro and nanotechnology for optical and high-frequency communications from XLIM Laboratory, Limoges, France in 2015. His research interests include antenna design.

Hassan Mehdi: He received the Ph.D in circuits, systems, and micro and nanotechnology for optical and high-frequency communications from XLIM Laboratory, Limoges, France in 2010. His research interests include system simulations.

Yaakoub Dia was born in Lebanon, in 1988. He received the Ph.D in circuits, systems, and micro and nanotechnology for optical and high-frequency communications from XLIM Laboratory, Limoges, France in 2016. His research interests include microwave filters.