Optical sensors for corrosion detection in airframes

P.G. Venancio a,b,c, R.A. Cotts d, R. Narayanaswamy e, J.C.S. Fernandes b,c,*

a OGMA, Indústria Aeronáutica de Portugal, 2615-173 Alverca, Portugal
b Department of Chemical Engineering, Instituto Superior Técnico, TULisbon, 1049-001 Lisboa, Portugal
c ICEMS, Instituto Superior Técnico, 1049-001 Lisbon, Portugal
d Corrosion and Protection Centre, The University of Manchester, Manchester M13 9PL, United Kingdom
e Centre for Instrumentation and Analytical Science, University of Manchester, Manchester M60 1QD, United Kingdom

ARTICLE INFO
Article history:
Received 23 July 2012
Received in revised form 28 February 2013
Accepted 14 March 2013
Available online xxx

Keywords:
Airframe corrosion
Sensors
Aluminium
Fluorescence

ABSTRACT
The use of sensors to detect aluminium corrosion in airframe structures could allow reducing significantly
the maintenance costs of fleets. An appropriate sensor may detect corrosion at an early stage, when the
removal of the corroded material from the original structure does not involve a structural repair. More-
over, by guaranteeing that corrosion is locally detected by an efficient sensor, the need for inspections
in some areas could be eliminated or, at least, inspection intervals could be increased, with significant
reduction of costs but still maintaining a conservative approach for aircraft safety.

In the present work an optical sensor is presented, that can be used to detect corrosion products inside
critical aircraft joints which are known to be very susceptible to corrosion. This sensor is based on the
remote detection of aluminium ions produced in the corrosion process. The proposed method for the
preparation of these sensors and the results obtained will be discussed.

1. Introduction

In recent years, optical fibre sensors had a considerable application in the field of health monitoring of structures in the aerospace, civil and marine industries. The ability of optical fibre sensors to monitor a variety of structural health indicators in different materials, such as advanced composites, concrete and metallic alloys, has been successfully demonstrated by many researchers trying to develop smart structures and systems [1–4].

The main advantages of optical fibre-based sensors include insensitivity to electromagnetic radiation (as no electrical signals are involved at the sensing region), spark free, light weight and minimal intrusiveness (due to their relatively small size) which are all properties needed for a sensor intended to be applied in an airframe.

Due to the small diameter, flexibility and ability of remote sensing, optical fibre sensors are an excellent option to monitor corrosion in hidden areas, like under sealant beads and lap joints (Fig. 1).

Inaccessible areas are hard to inspect and most traditional non-destructive inspection methods require 5–10% section loss of material for corrosion to be detected [5,6]. So, by the time the inspection indicates corrosion, its extent is already too severe, leading to an inevitably expensive repair or replacement of the component.

Developing an optical fibre sensor that could detect corrosion at an early stage would be an effective tool to reduce costs of aircraft maintenance, reducing, at the same time, the risk of an unexpected structural failure by corrosion degradation.

Optical fibre sensors are already a mature technology, being currently used on airframe monitoring. Optical fibre Bragg grating sensors (FBG) [7–10], which are already commercially available, are commonly used on structural health monitoring systems, to monitor several parameters such as strain, temperature and vibration [10]. Optical fibres have also been used to follow the life cycle of a composite material [11]; sputtered aluminium on an optical fibre is used to follow corrosion in an adjacent structure [4,12,13]; electroless deposit of copper on a optical fibre is used also to follow corrosion in structures [14]; optical pH sensors are used to monitor the variation of pH in particular areas and consequent evolution of corrosion [3] and fluorescent fibre optic sensors are used to detect corrosion products [5].

The optical sensors developed up to now for aluminium alloys [4,12–14] are based on the detection of the corrosivity of the environment. They normally involve the use of materials which are different from the aluminium alloys used in the airframe, such as pure aluminium, electroless deposited Ni–P or copper, and the degradation of these materials is then correlated with the expected degradation of the parent structure. However, the mechanisms of corrosion degradation for the sensor material and for aluminium...
alloys are often different, so a reliable relation between the sensor output and the parent structure degradation is difficult to obtain. In the present case, the proposed sensor will detect the presence of corrosion products, which is a direct measurement and a quite different approach. An optical sensor with a similar working principle has been developed by McAdam et al. [5] but the polymer used in the frame of the present work is different and has been optimized in order to enhance the polymer/silica fibre bonding which is of extreme importance for the real conditions reliability of the sensor.

1.1. Fluorescence/MIP and MNIP based recognition technology for aluminium ions

A Molecularly Imprinted Polymer (MIP) is a polymer that is formed in the presence of a molecule that is extracted afterwards, thus leaving complementary cavities behind. These polymers show a certain chemical affinity for the original molecule and can thus be used to fabricate sensors, on catalysis or for separation methods. A Molecularly Non-Imprinted Polymer (MNIP) is a polymer that already has a chemical affinity for a molecule or ion, without the need of being previously synthesized in the presence of the mentioned molecule or ion that is extracted afterwards.

There are two major approaches to manufacture ion-selective imprinted polymers based on metal ion coordination phenomena [15]: one approach is based on the molecularly imprinting process to obtain the final geometric arrangement needed for the complexation of a specific ion; the other option (used in both MNIP and MIP) is to use a chelator that already has geometric constraints predisposed to a certain metal ion size or coordination geometry and in this case, when used, the subsequent imprinting process is only used to make small changes in the geometry to enhance selectivity.

Recent developments in MIP technology as sensing receptors [16–21] have made them a viable and mature solution to be integrated as a fluorophore into fluorescent optical sensors.

Most aircraft components are manufactured from aluminium-based alloys; therefore if the objective is to detect corrosion in an early stage, the fluorescence optical sensors developed must be focused on the detection of by-products of the corrosion of aluminium alloys. For example, for aluminium alloys the indication of corrosion should mainly result from the detection of aluminium cations, normally formed during the corrosion of the alloy. Due to the limited solubility of most elements in aluminium, the alloying elements of AA 2024 T3 are mainly located in second phase precipitates. The main corrosion processes in AA 2024 T3 are related with dissolution of aluminium from the matrix or from S-phase (Al2CuMg) [22]. Thus, the ability of detecting aluminium ions will be a mandatory characteristic for the development of an optical sensor with the objective of detecting corrosion products of AA 2024 T3.

Several works were found in literature where sensors have been developed to detect aluminium cations using fluorescence techniques [16,17,23], including optical fibre sensors [5,21]. The stability of the complex formed between the fluorophore and the analyte depends on the nature of cation, nature of solvent, temperature, ionic strength and pH [24].

The ion recognition and complex selectivity of a fluorophore is of major importance to design an efficient fluorescent sensor, particularly when other cations are also present in the micro-environment to be monitored. In “real-life” the presence of other ions in the environment is impossible to avoid and must be taken into account. The MIP/MNIP selectivity depends on the characteristics of the fluorophore, such as the ligand topology, the number and the nature of the complexing heteroatoms or groups, which must match the characteristics of the cation, such as ionic diameter, charge density, coordination number and intrinsic nature, according to the principles of supramolecular chemistry [25].

1.2. Lap joints

Lap joints are applied throughout the aircraft, since they are the most efficient method to connect structural parts in order to transfer the load correctly between them. A typical fuselage section, with several lap joints connecting the skins between them and to the inner aircraft structure is presented in Fig. 2.

Although riveted lap joints are the most common in an airframe, lap joints can also consist of two or more pieces of overlapping material joined together by spot welding or adhesive. The main issue for this structural component is the difficulty of inspecting the mating or faying surfaces.

Mechanical joints are probably the most common source of failure in an aircraft structure [26] due to corrosion degradation or fatigue failure, and therefore their design is of extreme importance, as is the ability to monitor them.

Most of the airframe structure is made from high strength aluminium alloys, protected by a corrosion protection system, as defined in T.O. 1–1–8 [27]. The typical protection system for an aluminium alloy airframe consists of a conversion coating (0.1–0.2 μm) or anodized layer (1–5 μm), a chromate-inhibited primer (15–45 μm) and a polyurethane topcoat (44–55 μm). In most inner airframe areas, the polyurethane topcoat is not applied since its main function is to protect the chromate primer from UV light degradation.
Additionally, a chromate-containing sealant is applied in the faying area of the riveted lap joints, into the fasteners and holes. The sealant has the important function of minimizing friction between components and between the rivet and the wall of its hole. The sealant also fills all the gaps in the lap joint in order to prevent the migration of moisture to these voids that otherwise could become highly aggressive localized microenvironments. Nevertheless, even with all these corrosion protection measures, lap joints are the most corrosion prone zones of an aircraft [28,29]. This is not only due to a higher corrosion rate compared to the rest of the airframe, but to the difficulty in detecting corrosion in an early stage inside the lap joint. An example of a lap joint where corrosion was not detected in time is shown in Fig. 3.

Riveted lap joints can be considered critical areas in an airframe, due to their geometry, materials, properties and functions. All these factors, working together, lead to a stress concentration around holes and fasteners, which, added to thermal cycles, will produce unavoidable damage in the corrosion protection coating, which will have a significant influence on the evolution of corrosion in the referred areas.

From previous studies [30], it is known that the corrosion initiation in the interior of a lap joint results in a change of pH and in the production of aluminium and magnesium ions. Both these ions can be detected using tailored and specific sensors [3,5,16–18,21,31–34]. Initiation and progression of corrosion inside a lap joint only occurs in the presence of a conductive medium. Usually, when the protection coatings and sealant are broken, the lap joint is exposed to a source of moisture, leading to the wetting of its interior. It was been demonstrated [35] that, due to capillary forces, the wetting process of a lap joint interior can continue even after the outer surface has been dried. The same authors also have verified through testing that, at room temperature, water penetration into the lap joint is rapid, but its egress from occluded regions is much slower.

This process tends to be aggravated in the presence of corrosion products inside the lap joint. It has been observed that, after being subjected to an accelerated corrosion test in aggressive environment, a lap joint may continue to show corrosion activity even after 4 days of continuous exposure to a dry environment. This is due to the capillary forces and osmotic effects that retain water in the occluded regions.

Due to their flight cycles and operation environment, aircraft have an unpredictable time of wetness of their airframe, which is highly dependent on the surrounding environment (humidity and temperature), meaning that, for aircraft operating in different conditions or climates, quite different corrosion behaviours can be found for the same lap joint.

The corrosion inside a lap joint can be more active than in the other areas of the airframe, but for this to happen it is mandatory that critical conditions exist inside the lap joint, meaning that the existing protection sealant must be cracked in order for water to ingress more easily into the lap joint interior. Without sealant degradation, the electrolyte will not be able to migrate into the inside of the lap joint and corrosion will not initiate. Moreover, sealant degradation may occur to different extents, depending on the location of the part in the aircraft, where some areas are more exposed to the environment elements or submitted to higher vibration and stronger loads than others. This is the main reason why lap joints consisting of the same materials, geometry and mechanical elements in an aircraft display different behaviours, some not showing any corrosion issues during their entire design life while others may suffer corrosion in a short time, sometimes even shorter than the OEM pre-defined time interval for the structural inspection of the area.

The objective of this work is to develop corrosion sensors tailored specifically to detect localized corrosion inside of a lap joint that are reliable, simple and cheap to manufacture. For the monitoring of lap joints, a sensor that can be introduced inside that occluded area is needed, as the corrosion may take place there. An optical fibre sensor is well-suited to perform this task. Thus, in this work optical fibre sensors for the detection of aluminium ions have been studied.

In order to be used in lap joints, optical fibres should have a diameter small enough not to compromise the normal performance of the joint. In fact, the proposed sensors can be produced with fibres of any commercially available size. Moreover, a lap joint in an aircraft is normally protected with a sealant in its faying surface. An optical fibre of 0.2 mm diameter may be easily located in that region, being covered by the sealant bead in order not to become a weak point for water ingress. Obviously, the sealant may crack during normal aircraft operation, due to several reasons (vibration, loading, thermal cycles), leading to water access to the joint, but this is exactly the current situation (and the one the is meant to be detected) and it is believed that it will not become worse by the insertion of the fibre.

The choice of an MIP or an MNIP as recognition compounds will depend on the field and nature of application. In the frame of this work, several recognition polymers (MIP and MNIP) were developed, using different fluorophores, in order to obtain the most suitable for the detection of AA 2024 T3 corrosion. Initially, the research was focused in the MIPs, but along the development process it was concluded that MNIPs could be a better option.

2. Experimental

2.1. Reagents and materials

Deionized (Millipore©) water and methanol (Aldrich) were used as solvents. For the synthesis of MNIP with 8-hydroxyquinoline derivate as a fluorophore, the following reagents were used as purchased: 8 hydroxyquinoline-5-sulphonic acid (8HQS), 8-hydroxyquinoline (8HQ), 8-hydroxy-2-quinolinecarboxylic acid (8HQCA), 8-hydroxy-2-quinolinecarboxaldehyde (8HQC), ethylene glycol dimethacrylate (EGDMA, 98%), acrylamide (97%) and 2-hydroxyl-ethyl methacrylate (HEMA, 98%), all from Sigma–Aldrich, and 2,2'-azobisisobutyronitrile (AIBN, 97%) from BDH.

Silica optical fibres from Avantes were used for the manufacturing of the probe. For the bonding of the polymer to the silica fibres, 3-(trimethoxysilyl)propyl methacrylate (MPS) and absolute ethanol, both from Sigma–Aldrich, were used in a surface modification pre-treatment.

To test the ability of the polymer (isolated and bonded to the optical fibre) to detect several ions, solutions with deionized water and the following reagents were used: magnesium sulphate (99.5%)
from Baker & Adamson, cupric sulphate (98.5%) from M&B, sodium sulphate (99%) from Panreac Quimica, calcium sulphate (99%) and potassium aluminium sulphate (99%) from Merck.

The coupons used in the preliminary test were made of aluminium alloy 2024-T3 (AMS-QQ-A 250/5) from AMI Metals, Inc.

2.2. Synthesis of molecular non-imprinted polymers

Several molecular non-imprinted polymers were synthesized, using solutions of different 8-hydroxyquinoline derivaties (8HQS, 8HQ, 8HQCA and 8HQC) as complexing ligands (fluorophores) for optical detection.

For the synthesis of the polymers, 5.0 mL of one of the solutions mentioned above was pipetted into a 25-mL borosilicate bottle and 0.1422 g (2 mmol) of acrylamide, 0.260 mL (2 mmol) of HEMA, 5.0 mL of EGDMA (25 mmol) and 0.1 g of AIBN were added. The mixture was stirred for 30 min, followed by purging with nitrogen for 10 min before being sealed. It was then transferred into a hot water bath for polymerization during several hours.

2.3. Evaluation of recognition compounds

2.3.1. Equipment

For the emission fluorescence characterization of each polymer developed, an AvaSpec 2048 fibre optic spectrometer and an AvaLight-XE xenon pulsed light source were coupled to a 1/2" industrial fluorescence probe (specific for the measurement of fluorescence in solids) that consists of 12 excitation fibres of 200 μm around a 600 μm measurement fibre, which takes the fluorescence signal back to the spectrometer. The software used for data treatment was AvaSoft-7.3 USB1. Both equipment and software were purchased from Avantes.

2.3.2. Procedure

For the evaluation and optimization of the synthesized recognition compounds excitation wavelengths of 350–380 nm were used. The tests were made in the presence of several solutions, containing different analytes such as Al³⁺, Cu²⁺, Mg²⁺ or Ca²⁺. The process of putting a solution in contact with the polymers was repeated in the same way during all the testing. After milling to powder, a small amount of polymer was deposited over a metal coated by a grey matte paint (MIL-C-85285) as shown in Fig. 4a. The matte paint has the function of minimizing the noise in the fluorescence measurements, because it will not reflect light by itself. Then, an Eppendorf pipette was used to apply a 25 μL drop of solution over the polymer (Fig. 4a) and the fluorescence evolution in this area was followed (Fig. 4b).

2.4. Manufacturing of optical sensors

Based on the results of the evaluation of recognition compounds, optical fibre sensors using a MNIP with 8-HQ as a fluorophore were developed.

Two types of optical fibres were first considered for the production of the sensors: PMMA fibres and silica fibres. However, although cheaper than the silica fibres, the PMMA fibres were not considered a good option for the production of sensors. Their high transmission loss for light in near UV range results in a strong attenuation of the excitation signal (350–380 nm), resulting in a very low emission of fluorescence. The silica fibres were then selected, although their use involves a conditioning step in order to increase the adhesion of the MNIP to the fibre.

Probes based in a glass fibre (silica) were manufactured and tested. The sensors were produced at the end of a multi-branch fibre bundle: the two fibres of that end (600 μm fibres) were embedded in the sensing polymer and the two branches on the opposite side (each one with one fibre), were connected to the light source and to the spectrometer (Fig. 5).

In order to bond to the polymer, the fibre tips were cut with a manual cleaver (Newport F-CL1). Then, the tip section was carefully polished with lapping films with the following sequence: 5 μm (SiC film), 3 μm, 1 μm and 0.3 μm (aluminium oxide films).

After being cut and polished, in order to obtain a flat surface, free of defects, the optical fibre tip was washed in a stirred pure ethanol solution for 2 h.

The surface of the fibre was then modified by immersion in an alcoholic solution of 3-(trimethoxysilyl)propyl methacrylate (MPS) in order to enhance its bonding to the polymer. The reaction proceeded for 48 h and then the tip was washed for 2 h in pure ethanol under vigorous stirring.

The MNIP using 8-HQ as fluorophore was synthesized and simultaneously bound to the fibre by thermally induced free radical polymerization. Initially, the fluorophore was dissolved in methanol and the mixture was stirred until becoming a transparent solution. This mixture was pipetted into a borosilicate bottle

---

**Fig. 4.** Apparatus and instrumentation (a) polymer deposited over the matt substrate; (b) layout of apparatus used for the fluorescence measurement.

**Fig. 5.** Optical sensor with multi-branch fibre bundle (silica fibre).
and 0.75 g of acrylamide, 0.130 mL of HEMA, 2.5 mL of EGDMA and 0.05 g of AIBN were added and stirred for 30 min. Meanwhile, the optical fibre was placed in a sealed cup and purged with nitrogen for 10 min in order to eliminate oxygen, as it can react with free radicals and terminate the polymerization process. In order to obtain a thin layer of polymer deposited on the tip surface, without becoming stuck to the remaining mixture, a syringe with the MNIP mixture referred above was inserted in the sealed cup and 0.5 mL of mixture were added, corresponding to the volume needed to cover the tip surface. The polymerization took 4 h, by maintaining the cup in a hot water bath. At the end of the process an opaque and thin layer of polymer was obtained on the fibre tip.

2.5. Testing of optical sensors

Sensors manufactured by bonding the MNIP to the silica optical fibre, as described above, were tested in individual solutions with different aluminium ion concentrations (10⁻² M, 10⁻³ M and 10⁻⁴ M).

The measurements were conducted by connecting one of the SMA-905 terminals of the multi-branch fibre bundle to the AvaLight-Xe pulsed xenon lamp and the other terminal to the AvaSpec-2048 spectrometer. The fluorescence intensity recorded in deionized water was subtracted from all results.

Preliminary trials tests have been performed in a salt spray chamber, using sensors embedded in riveted lap joints, to check for their ability to detect corrosion onset.

3. Results and discussion

3.1. Evaluation of recognition compound

As mentioned above, several recognition polymers (MIP and MNIP) were developed in the frame of this work, using different fluorophores, as referred in the experimental part, in order to obtain the most suitable for the desired application. Initially, the research for the development of the recognition polymers was focused in the MIPs, but along the development process it was concluded that a MNIP was a better option. Thus, the recognition polymers presented in this paper always consisted of MNIPs, using different fluorophores, all of them 8-hydroxyquinoline derivates, whose fluorescence behaviour in several conditions was analysed.

The first fluorophore tested was 8HQ, already used by Muk [23] for a similar application (detection of aluminium ions in a flow cell). However, the major drawback for the use of 8HQ as a fluorophore is its tendency to easily dissolve in water. Since the fluorophore is not bound by a covalent bond to the polymer matrix, but entrapped in the referred matrix, there is a high probability of the 8HQ being washed away from the polymer when submitted to several wet/dry cycles, as happens in an airframe. This was confirmed by testing, as shown in Fig. 6, where the effect of washing 8HQ-based MNIP in water on its fluorescence spectra is presented.

From the structure of 8HQ, it may be observed that a hydroxyl group and a nitrogen, available to form complexes with the metal ions, continue to exist, in the same way as in 8HQ. The lack of a sulphonic acid group, present in 8HQ, allows 8HQ to have a higher solubility in methanol than other 8-hydroxyquinoline derivatives, allowing a higher concentration of fluorophore in the MNIP matrix. On the other hand, this compound is insoluble in water, which eliminates the problem of leaching of the fluorophore by water.

The fluorescence spectra of a MNIP with 8HQ as fluorophore, in the presence of different concentrations of aluminium ions, are shown in Fig. 7. The fluorescence peak intensities obtained at 550 nm clearly increase with the concentration of aluminium, as depicted in Fig. 8, where, a linear correlation is found between the intensity and the logarithm of the aluminium concentration.

According to Kelly et al. [36], who have analysed several corroded lap joints from different aircraft, the solutions formed in a corroded lap joint have an average Al³⁺ concentration of 1.8 × 10⁻³ M. Thus, the 8HQ based recognition polymer shown above has the desired accuracy for detecting the existence of corrosion in a lap joint, as required.

The effect on the fluorescence properties of the 8HQ-based MNIP of other ions that are present in a corroded lap joint environment was tested, using solutions of Al³⁺, Mg²⁺, Cu²⁺, Na⁺ or Ca²⁺, each with a concentration of 10⁻³ M.

![Fig. 6. Emission spectra in the presence of 0.01 M Al solution (excitation range of 350–380 nm) for 8HQ-based MNIP as produced and after being washed with water (baseline subtracted).](image)

![Fig. 7. Fluorescence intensity evolution of 8HQ-based MNIP in the presence of different concentrations of aluminium ion (baseline subtracted).](image)

![Fig. 8. Dependency of the fluorescence intensity at 550 nm with aluminium ion concentration for an 8HQ-based MNIP.](image)
Through the analysis of Fig. 9 it is observed that, besides Al³⁺, both Mg²⁺ and Ca²⁺ induce fluorescence of the MNIP. However, the fluorescence peaks that correspond to each ion are located at different wavelengths. The Mg²⁺ and Ca²⁺ fluorescence peaks are considerably wide, leading to some overlap with the Al³⁺ fluorescence band. However, the much higher intensity of the Al³⁺ fluorescence peak in the 530–550 nm range, still allows the detection of this ion and the separation of its contribution from those of Mg²⁺ and Ca²⁺. The Na⁺ and Cu²⁺ ions did not show any fluorescence.

From these results it may be concluded that, even in the presence of other ions, the fluorescence peak due to the presence of aluminium ions may be distinguished from the other. Moreover, if the detection wavelength is set in the range of 530–550 nm, the signal will be considered as almost independent from the presence of other ions.

As mentioned above, the corrosion of an aluminium alloy of the 2XXX series results in the release of Al³⁺, Cu²⁺ and Mg²⁺. So, the detection of the later two ions could be, in principle, helpful as an indication of the existence of a corrosion process. In the case of Cu²⁺, this ion does not induce any fluorescence of the MNIP, but for Mg²⁺ a strong signal is found. Thus, the presence of magnesium cations in the lap joint environment and their detection was assessed with more detail. Magnesium solutions with the same concentrations as for the aluminium cations (i.e., 10⁻⁴ M, 10⁻³ M and 10⁻⁴ M) were used. From the fluorescence spectra depicted in Fig. 10 it can be concluded that the MNIP is sensitive to the presence of magnesium. An increase in magnesium concentration from 10⁻⁴ M to 10⁻³ M leads to an increase of the emission intensity but the same is not seen from 10⁻³ M to 10⁻² M. One possible reason for this behaviour may be the saturation of the MNIP, whose sites available for bonding to the Mg²⁺ ions could become fully occupied by these ions. In fact, besides the effect of different coordination numbers of Mg²⁺ and Al³⁺ complexes, the ionic radius of Mg²⁺ (0.72 Å) is higher than that for Al³⁺ (0.53 Å), meaning that some of the sites available for Al³⁺ bonding may be too narrow to accommodate the Mg²⁺ ion.

The average concentration of magnesium ions determined by Kelly et al. [36] in a corroded lap joint was 8.8 × 10⁻² M. This value can be considered as very high, when compared to the concentration of Al³⁺ in the same environment (1.8 × 10⁻³ M) especially if the composition of the AA 2024-T3, where the percentage of magnesium spans from 1.2% to 1.8% and that of aluminium ranges from 92.3% to 96%, is taken into account. Although the formation of aluminium hydroxide may leave less free aluminium ions available in the solution, explaining the lower concentration in the corrosive environment, it is difficult to accept that the Mg²⁺ concentration could be much higher than the Al³⁺ concentration, if both ions result from the corrosion of AA 2024-T3. Thus, another source of magnesium ions may be responsible for their release to the solution and, in fact, most primers used in the aeronautic industry include magnesium salts in their formulation, which may leach out of the paint coating when corrosion begins. However, even in this case the presence of Mg²⁺ in the lap joint solution will be indirectly related to the formation of corrosion. Thus, it is clear that the fluorescence response due to magnesium may also be considered as a good indication of the onset of corrosion.

In “real life”, when a MNIP sensor is put in a lap joint, it will be in contact with a solution where the ions mentioned above compete against each other for the available sites to bond in the MNIP. To evaluate this effect, the response of the MNIP to a solution containing all the referred ions (Al³⁺, Mg²⁺, Cu²⁺, Na⁺ and Ca²⁺) with the same concentration (10⁻³ M) and to a solution with all ions except Al³⁺, was compared, as shown in Fig. 11.

The fluorescence spectrum for the solution without aluminium ions shows the fluorescence peaks of the magnesium and calcium ions, whereas in the presence of aluminium the spectrum only shows the characteristic fluorescence peak of this element. The results imply that the MNIP preferentially bonds to the aluminium ions compared to the other ions existing in the solution, so their presence is not deleterious to the detection of aluminium. The demonstrated high selectivity of the developed MNIP allows its use as a recognition polymer in a sensor to be used as a monitoring system inside of a lap joint.

A solution inside a lap joint is not in a steady state, its composition changing with time, in particular after the initiation of corrosion. As it was shown above (Fig. 9) from the different ions found in a lap joint environment, only Ca²⁺, Mg²⁺ and Al³⁺ promote the fluorescence of the 8HQ MNIP. Before the initiation of corrosion,
the concentration of aluminium ions is expected to be very low, but small concentrations of Ca$^{2+}$, Mg$^{2+}$ (this one resulting from leaching of the chromates primer), Na$^+$ and Cu$^{2+}$ may already be present. The onset of corrosion will lead to the release of Al$^{3+}$ and that should be the event that triggers the sensor. In order for a successful detection of Al$^{3+}$, the MNIP should have enough available sites for the bonding of this ion, so it is important to ensure that these sites are not fully occupied by the other ions pre-existing in the lap joint environment. With the aim of testing this condition, the MNIP was initially exposed to a solution with Ca$^{2+}$, Na$^+$, Mg$^{2+}$ and Cu$^{2+}$, each one in a concentration of 10$^{-3}$ M, and its fluorescence spectrum was measured. Then, after 12 h, Al$^{3+}$ with a concentration of 10$^{-3}$ M was added to this solution and the fluorescence spectrum was measured again. Through the analysis of the emission spectra evolution (Fig. 12) it is concluded that the presence of aluminium ions is detected even if the MNIP has been previously exposed to other ions that may complex with 8HQ, meaning that enough available sites remain for the bonding of aluminium ions. This verification is of crucial importance to allow the use of this MNIP inside a lap joint.

3.2. Testing of optical sensor

Sensors manufactured by bonding the MNIP to the silica optical fibre, as described in experimental section (Fig. 13) were tested in individual solutions with different aluminium ions concentrations (10$^{-4}$ M, 10$^{-3}$ M and 10$^{-2}$ M). The respective fluorescence emission behaviour is shown in Fig. 14, corresponding to the presence of a peak at ca. 550 nm, as found in the tests of the MNIP, and the increase in the aluminium concentration is clearly reflected in the increase of the fluorescence intensities.

From these results, the silica sensors based in 8HQ MNIP have proved to adequately detect the presence of aluminium ions and are considered as viable sensors for being used in lap joints.

Preliminary tests of sensors embedded in lap joints, in a salt spray chamber, have shown their ability to detect the onset of corrosion under the sealant bead.

4. Conclusions

Optical sensors, based in fluorescence emission, may be used in the detection of specific ions, such aluminium, indicating the onset of corrosion of an aluminium alloy. Fibre optics technology is adequate for the production of sensors that may be placed in occluded areas, such as the lap joints in an aircraft. Their small size and flexibility are essential for that application.

8-Hydroxyquinoline (8HQ) was considered the best fluorophore for detection of aluminium using a MNIP. This is mainly due to its solubility in methanol (the solvent used in the production of the MNIP), allowing to reach high concentrations in the resulting MNIP, whereas its solubility in water is very low, avoiding its progressive leaching to the environment upon use. According to the tests carried out with this sensor, it shows an adequate sensitivity to the aluminium ions and its detection properties are not much influenced by the presence of other ions, such as Ca$^{2+}$, Na$^+$, Mg$^{2+}$ and Cu$^{2+}$. Further studies will be needed to assess the specific effect of each one of these ions on the fluorescence behaviour of Al$^{3+}$ in the selected wavelength.

The next step of this study will involve the use of field trial, in order to optimize of the sensor setup, defining limiting parameters such as the maximum length of the optical fibre for appropriate detection of fluorescence, as well as to evaluate the sensor’s performance for the detection of AA2024-T3 airframe corrosion in real conditions.

Acknowledgements

The Portuguese Science and Technology Foundation (FCT) is acknowledged for the financial support under PhD grant SFRH/BD/15586/2006 (P. Venâncio).

The authors would also like to thank Prof. J.M. Gaspar Martinho, C. Baleiço and A. Fedorov for the fruitful discussions.

References

Inhibitors, Ni–P, and imprinted M. Z. G. M. S. D. K. S. Szunerits, Ghandehari, of Vukmirovic, Murray, Niu, (2007) 74–31–39. Bragg of Li, W. Wallbrink, An recognition of Aerospace Shimizu, T. Yan, 131 of Aerospace Sensors and Actuators 1 B 75 (2001) 1–4. C.D. Dealloying 251–258. Zhigang, Mouritz, in: International Science of Aircraft, graduating in 1967, specialising in Metallurgy, he was awarded a PhD in 1973 for work on electrodeposition in the fluidized electrode at the Department of Metallurgy and Materials Science at Cambridge. He was appointed as a Project Manager, then Research Manager at the Fulmer Research Institute, a contract research organization that was wholly owned by the Institute of Physics. There he worked on long-term research in the general area of corrosion, with much of the work being on corrosion fatigue. In addition he undertook many short-term failure investigations and other consultancy work. He joined the Corrosion and Protection Centre, UMIST in 1979, initially as a lecturer, then senior lecturer (1992) and reader (2000). He was active in the development of teaching in the field of Corrosion, being responsible for the development of a distance learning approach to the MSc in Corrosion Control Engineering, and Director of the ECTL P. consortium that developed the ECTL courseware to support corrosion teaching. He is founding editor of the open access online Journal of Corrosion Science and Engineering and founder of the CORROS-L Mailing List for corrosion questions. In 2005 he was awarded the T. J. Hull Award of NACE International for services to NACE in the field of publications.

Ramaier Narayanaswamy is currently an academic visitor in the School of Chemical Engineering and Analytical Science (CEAS) at the University of Manchester. He retired as a reader from this University in September 2010. He obtained his PhD in 1989 from the University of Dundee (UK) in Analytical chemistry and DSc in 1995 (University of London) in Analytical Chemistry. Previously he was a lecturer in Chemistry at the University of Sri Lanka, Peradeniya, Sri Lanka (1967–1978), and a Postdoctoral Research Fellow at the University of Southampton, UK (1978–1981) and the University of Warwick, UK (1982). He joined DIAS, UMIST, UK, in 1983 as a senior postdoctoral research associate and became the manager of the Optical Sensors Research Unit (1984–1987) and lecturer in instrumentation and analytical science (October 1984 to July 1990). He led the research group that deals with the fundamental and applied studies in molecular spectroscopy and in optical chemical sensors, biosensors and instrumentation. He has supervised PhD research of 30 postgraduate students and has over 175 publications including chapters in several books. He has also edited a book on Optical Sensors published by Springer in 2004.

João Salvador Fernandes (PhD in Chemical Engineering, Instituto Superior Técnico, 1997, Graduation in Chemical Engineering, Instituto Superior Técnico, 1987) joined IEST, the Engineering School of the Technical University of Lisbon, in 1987. He is a professor at the Department of Chemical Engineering. His main scientific interests are in the fields of corrosion and electrochemical techniques, with special relevance to Electrochemical Impedance Spectroscopy. He is involved in several national and EU funded projects in the fields of surface coatings, surface modification and biomaterials, where several electrochemical and surface analysis techniques are used for the assessment of the corrosion properties.

Biographies

Paulo Venâncio graduated at IST, Technical University of Lisbon, and received his PhD in Chemical Engineering at IST in 2012, under the supervision of Prof. João Fernandes. He is a design engineer of structures at the Design Office of OCMA and has 9 years of experience in the aeronautic industry at aircraft maintenance, manufacturing and design, being always involved in the fields of materials science and structures.

Bob Cottis is currently an Emeritus Professor in Corrosion Science and Engineering at the University of Manchester. He studied Natural Sciences at the University of Cambridge, graduating in 1967, specialising in Metallurgy. He was awarded a PhD in 1973 for work on electrodeposition in the fluidized electrode at the Department of Metallurgy and Materials Science at Cambridge. He was appointed as a Project Manager, then Research Manager at the Fulmer Research Institute, a contract research organization that was wholly owned by the Institute of Physics. There he worked on long-term research in the general area of corrosion, with much of the work being on corrosion fatigue. In addition he undertook many short-term failure investigations and other consultancy work. He joined the Corrosion and Protection Centre, UMIST in 1979, initially as a lecturer, then senior lecturer (1992) and reader (2000). He was active in the development of teaching in the field of Corrosion, being responsible for the development of a distance learning approach to the MSc in Corrosion Control Engineering, and Director of the ECTL P. consortium that developed the ECTL courseware to support corrosion teaching. He is founding editor of the open access online Journal of Corrosion Science and Engineering and founder of the CORROS-L Mailing List for corrosion questions. In 2005 he was awarded the T. J. Hull Award of NACE International for services to NACE in the field of publications.