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Interactions between marine microorganisms and metal: the start point of a new bioinspired solution for corrosion protection

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Abstract. Among the strategies currently used to protect metallic materials from corrosion, and thus increase their durability, conversion treatments and coatings can be considered as the most efficient and cost-effective alternatives. However, these techniques must comply with increasingly stringent regulations such as REACH. On another note, in the field of interactions between microorganisms and conductive material, it has been shown that microorganisms can not only accelerate corrosion in some cases (biocorrosion or MIC) but also inhibit it in others, thus protecting the underlying material (MIC Inhibition). In this context, the MICOATEC ANR project is based on the observation that interactions between an aluminium alloy (AA5083) and microorganisms in the marine environment lead to the formation of a protective layer against corrosion. The MICOATEC project aims to develop, via a biomimetic strategy, a new type of process for producing anti-corrosion coatings. The main goal is therefore to translate the natural biotic process into an abiotic technological process for corrosion protection, without replicating the biofilm itself or incorporating active biocompounds into the coating matrix.

Keywords: aluminium alloy / marine microorganisms / surface modifications / bioinspired process / anticorrosion solution

Résumé. Interactions entre les micro-organismes marins et le métal : le point de départ d'une nouvelle solution bio-inspirée pour la protection contre la corrosion. Parmi les stratégies actuellement utilisées pour protéger les matériaux métalliques de la corrosion, et ainsi accroître leur durabilité, les traitements de conversion et les revêtements peuvent être considérés comme les alternatives les plus efficaces et les plus rentables. Ces techniques doivent cependant respecter une réglementation de plus en plus contraignante telle que REACH. Par ailleurs, dans le domaine des interactions micro-organismes/matériaux conducteurs, il a été mis en évidence que non seulement les micro-organismes peuvent dans certains cas accélérer la corrosion (biocorrosion ou MIC) et dans d'autres l'inhiber protégeant alors le matériau sous-jacent (MIC inhibition). Dans ce contexte, le projet ANR MICOATEC repose sur le constat que les interactions entre un alliage d'aluminium (AA5083) et des micro-organismes du milieu marin conduisent à la formation d'une couche protectrice contre la corrosion. Le projet ANR MICOATEC ambitionne de développer, via une stratégie biomimétique, un nouveau type de procédé pour produire des revêtements anticorrosion. L'objectif principal est donc de traduire le processus biotique naturel en un processus technologique abiotique pour la protection contre la corrosion, sans reproduire le biofilm lui-même ni incorporer des biocomposés actifs dans la matrice du revêtement.

Mots clés: alliage d'aluminium / micro-organismes marins / modifications de surface / procédé bio-inspiré / solution anticorrosion

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1 Introduction

Among the strategies employed to protect metallic materials, conversion treatments and coatings can be considered as the most successful and cost-effective alternatives to efficiently increase the service lifetime of metallic structures [1–5], particularly for industrial applications in which the products are exposed to changing and hard weather conditions such as shipbuilding, automobile, aerospace, marine and oil and gas energy infrastructures. In this context of severe environmental conditions and increasingly constraining regulations, the surface treatment and coating industry sector is driven to develop more sustainable and ecofriendly solutions [6–13].

In the last decades, new emerging microbial-based technologies have been proposed following the development of more environmental friendly anti-corrosion solutions to increase longevity of structural metals. The fact that microorganisms can influence corrosion behaviors in an advantageous way, the so-called MICI (microbiologically influenced corrosion inhibition) [14–17] have opened different lines of research, synthesized in [18–20]:

- incorporation of active biomolecules as functional compounds in coating matrix, to implement corrosion inhibitory capacity of microorganisms and their metabolites;
- creation of surfaces integrating the behavior/properties of the living organisms on the metallic substrate, as biomimetic objects.

Notwithstanding the significant advances in both lines, the development of these new biological treatments continues at the laboratory level, with limitations for transfer to application in a real environment, considering the difficulties associated not only with the stabilization of microbial activity but even with the receptivity of the surface treatment and coating industry toward the use of microorganisms and even biocompounds.

In recent years and as a result of metal corrosion studies in marine environment, a new approach for microbial corrosion inhibition became relevant. This is the case for biomineralization. The evidence that the outcome of interactions between microorganisms and metal surface can result in an efficient protective layer increasing the metal corrosion resistance has been reported for the Al-Mg alloy for prolonged exposure in field conditions [21,22] and, recently, also in studies at laboratory level [23–25]. Figure 1 shows the SEM surface and cross-sectional morphology observations of an Al-Mg alloy after immersion in biotic and abiotic marine environment. The images indicate, in seawater that contained microorganisms, the formation of a compact and uniform layer on the Al alloy surface, which thickness increases with time. In contrast, in absence of microorganisms, the cross-sectional image shows localized corrosion of the Al-Mg surface [21,22]. Additionally, the Al-Mg surface exposed in biotic conditions presented a resistance to the charge transfer (measured by electrochemical impedance spectroscopy [EIS]) at least 2000 times higher than the surface exposed in abiotic conditions [26].

Considering this finding and being aware of the potential of this microbial induced mineralization phenomenon, the MICOATEC project established a new approach for the development of a bioinspired anticorrosion solution. The main goal is to translate the natural biotic process into an abiotic technological process for corrosion protection, without replicating the biofilm itself or incorporating active biocompounds into a coating matrix.

To reach the above-mentioned main objective, the project will encompass two specific phases (Fig. 2):

- phase 1 – fundamental understanding of the natural formation mechanisms of a protective layer: the evolution of the chemical and physical characteristics of the naturally formed layer on the metal surface, during marine exposure, and the associated corrosion protection properties will be determined and analyzed in correlation with the microbial colonization/activity;
- phase 2 – mimicking the natural process to develop new abiotic anticorrosion solutions: the understanding of the natural process will be used to transform the biotic conditions into abiotic ones to achieve the replication of the protective solution. Two ways will be explored according to the involved phenomenon: reaction with the surface or deposit on the surface. New electrolyte compositions, new coating formulation and new experimental conditions are expected as main MICOATEC output.

The present work shows the initial results of phase 1 of MICOATEC project, which is the outcome of the first natural immersion test performed in the Mediterranean Sea (C1 campaign). Several samples of Al-Mg (AA5083) were immersed at Genoa Outdoor Experimental Marine Station (GEMS) for different periods of time (15 days, 1 and 2 months). The main objective of this first field test was to understand the mechanisms of formation of the protective layer on the aluminium alloy surface. More specifically, to assess the evolution of the naturally formed layer during short immersion exposure, allowing the correlation between the physico-chemical characteristics and the anti-corrosion properties, determining the influence of marine microbial activity (bacteria, algae, etc.) on the process of aluminum alloy corrosion inhibition.

2 Materials and methods

2.1 Materials and preparation

AA5083 H-111 aluminium alloy (Al-Mg) was supplied by the Comptoir général des métaux, Cugnaux, France. The sheets acquired, with 1 and 7 mm of thickness, were cut into test samples of 10 cm × 20 cm.

2.2 In situ marine exposure

The marine immersion tests have been carried out on the platform available at the CNR-IAS Genova Experimental Marine Station (GEMS), located within the Port of Genoa, Genoa, Italy (Fig. 3). A set of 24 samples for each thickness

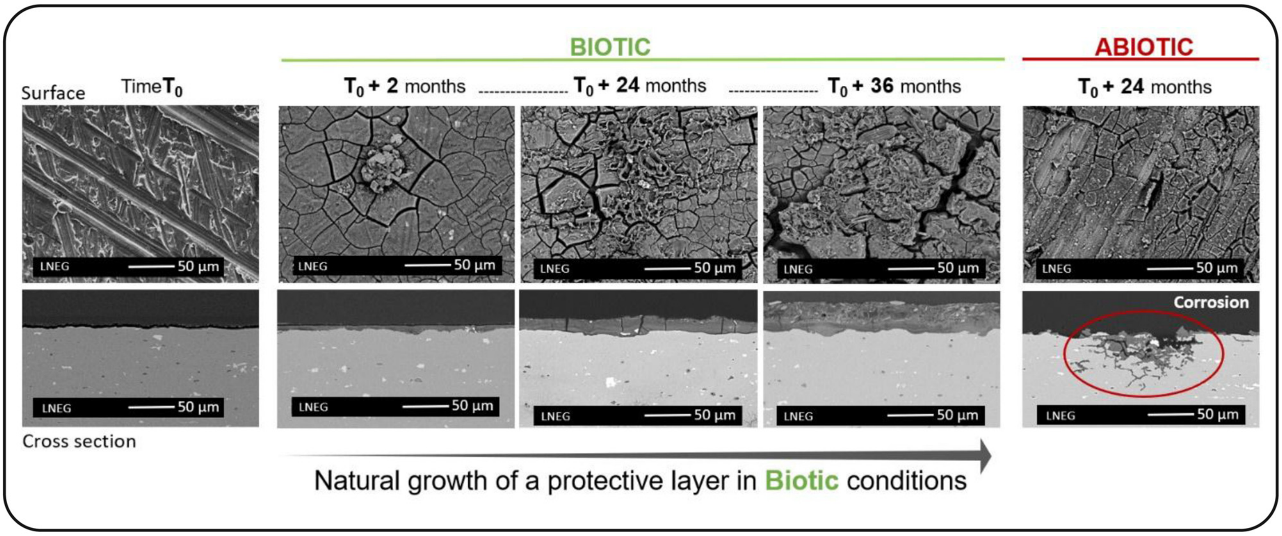

Fig. 1. Scanning electron microscope (SEM) images, surface and cross-section, of the AA5083 alloy after exposure in marine, biotic and abiotic environments [21,22].

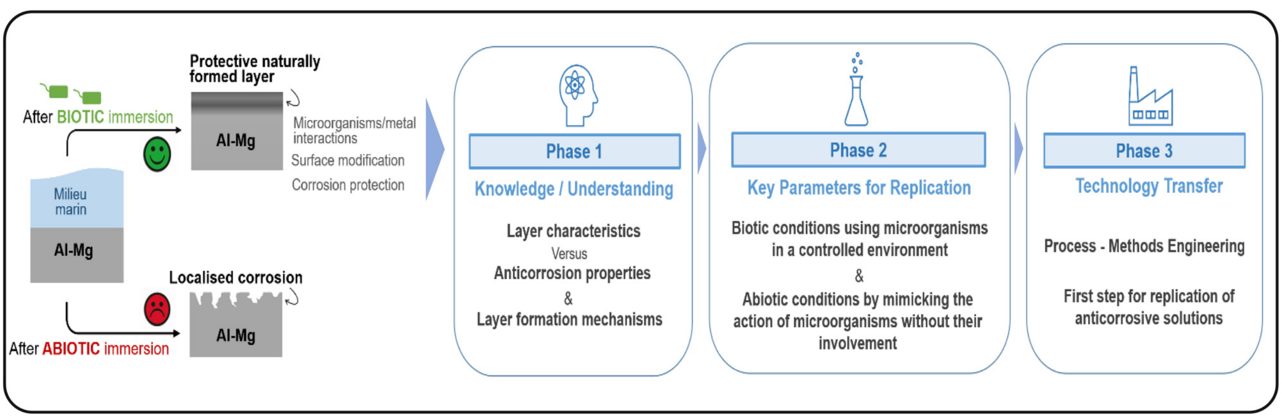

Fig. 2. MICOATEC approach and methodology

(1 and 7 mm) of aluminium alloy were immersed, and gradually recovered after 15 days, 1 and 2 months of exposure.

The C1 campaign started on September the 1st and finished on November the 2nd of 2020, after 60 days of immersion in natural Mediterranean Seawater.

2.3 Characterization after immersion

At the end of each time of exposure, 15 days, 1 and 2 months (Fig. 4), the surface samples were cleaned and dried in cold air, being subsequently observed and analyzed with the goal to assess the impact of the marine microbial activity (bacteria, algae, etc.) on the corrosion behaviour of the aluminium alloy.

2.3.1 Digital microscopy

The AA5083 samples of the C1 campaign were observed with a DVM6 Leica digital microscope before and after biofouling removal of the surfaces.

2.3.2 Scanning Electron Microscopy (SEM) with energy dispersive X-ray analysis (EDX)

After biofouling cleaning, the aluminium alloy samples immersed during distinct time of exposure were characterized, surface and cross-section, by SEM/EDX. The SEM observations were performed using a Philips FEG-SEM, mode XL30 microscope coupled with a Pathfinder Thermo Fisher Scientific energy dispersive X-ray spectrometer (EDX) for elementary chemical analysis. The cross-section samples were prepared using a cold mounting epoxy resin.

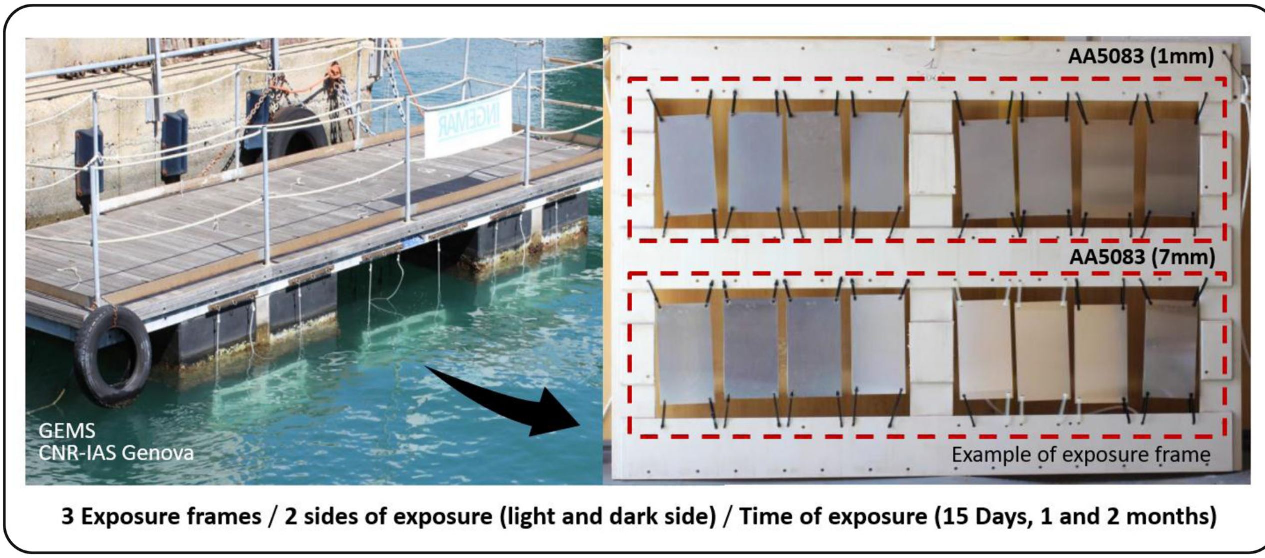

Fig. 3. MICOATEC first immersion campaign in Mediterranean Sea at Genova Experimental Marine Station CNR-IAS.

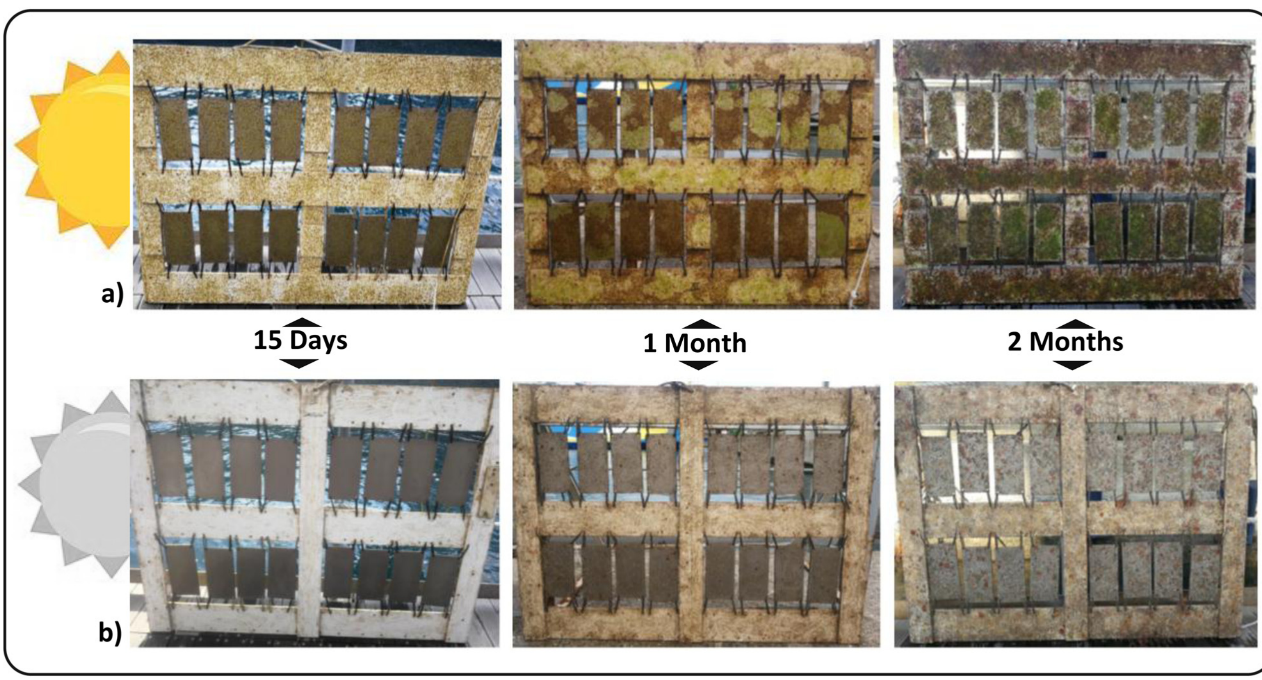

Fig. 4. MICOATEC C1 samples removed from Genova immersion platform (15 days, 1 and 2 months). Two side of exposure: (a) light side and (b) dark side.

Before observations surface and cross section samples were coated with a sputtered layer of gold (Au) to reduce charging effects.

3 Results and discussion

The visual inspection globally performed on AA5083 samples immersed for 15 days, 1 and 2 months, before and after biofouling cleaning, allowed to verify a reproductive behavior for both thickness of the aluminium alloy tested (1 mm and 7 mm). In this context, the results presented below are relative to the Al-Mg samples with 1 mm of thickness, after 15 days, 1 and 2 months of immersion (Fig. 5).

Figure 5 reveals the evolution of biofouling coverage on the Al-Mg surface with immersion time and the different behavior between the light and dark sides of exposure. At the end of 2 months of immersion, it can be found evidence of both micro- and macrofouling on the Al-Mg surfaces. The light side of exposure shows the presence of a soft fouling (example of non-calcareous fouling organisms, as seaweed, hydroids, tunicates, algae...), contrary to the dark

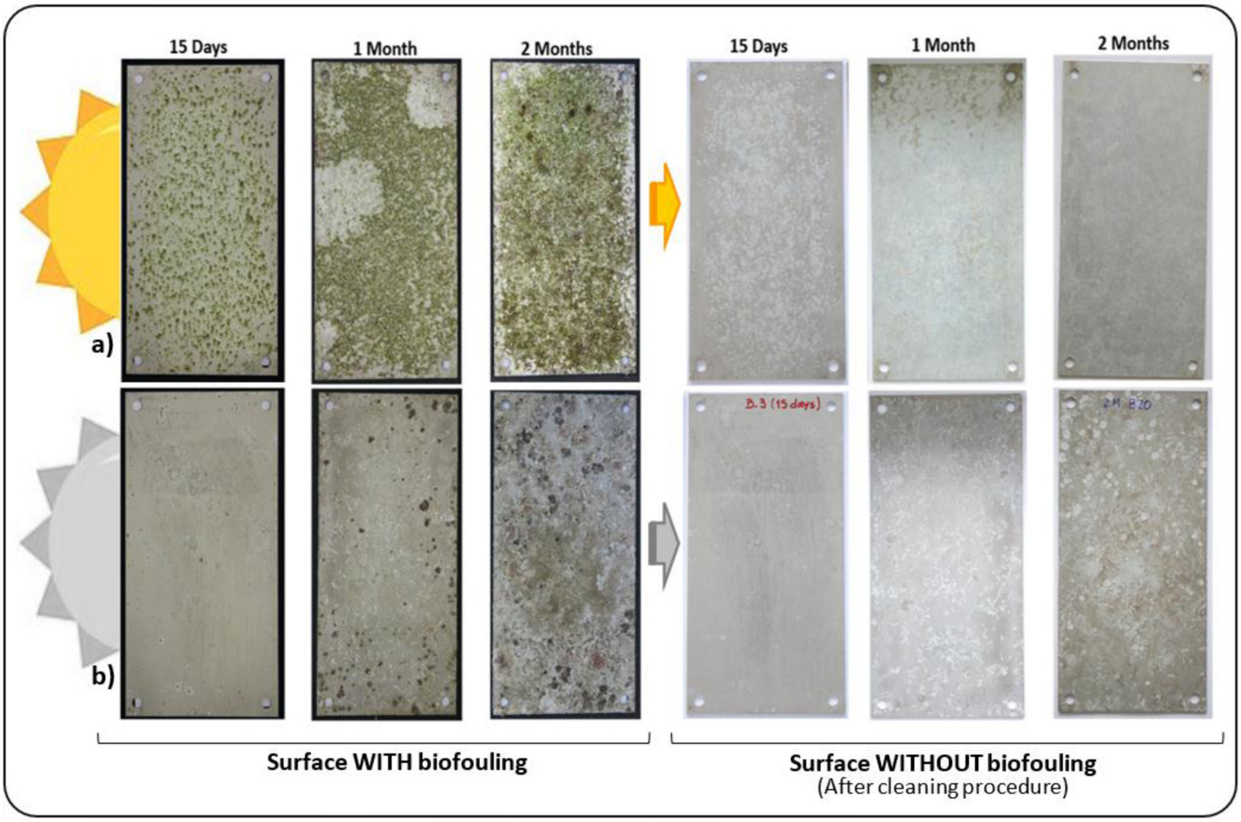

Fig. 5. Digital photographs of Al-Mg samples (10 cm × 20 cm), after 15 days, 1 and 2 months of immersion, light (a) and dark (b) sides of exposure, before and after biofouling removal.

side of exposure, which reveals the presence of a harder fouling (example of calcareous fouling organisms, including barnacles, tubeworms, mussels...)

After cleaning the samples, it was possible to verify that the distinct fouling community observed on the Al-Mg samples at the end of the immersion tests, light and dark side, respectively, has led to different surface modifications.

3.1 Digital microscopy

Figures 6 and 7 show the results of the digital microscope observations of the AA5083 samples, after different time of exposure, before and after removing the biofouling from the surface.

As mentioned above, different typology of biofouling developed on the aluminium alloy surfaces during the immersion time according to the exposure side (Fig. 6). The images of the Al-Mg surface exposed to the light side (Fig. 6a), revealed different species of algae (green, brown and red), whose presence was consolidated with the immersion time. The presence of a few calcareous tube made by tube worms was also observed. Oppositely, on the dark side (Fig. 6b), the presence of algae on the aluminium alloy surfaces showed to be significantly lower, being essentially visible the presence of calcareous tube made by tube worms, sponges and barnacles.

After the biofouling cleaning procedure (Fig. 7), it was possible to observe the different Al-Mg surface modifications occurred on each side of exposure, light and dark, respectively. On the light side (Fig. 7a), up to 2 months of immersion, no localized attacks were observed, contrary to the dark side (Fig. 7b) were random pitting corrosion of Al-Mg surface was observed after 2 months of exposure.

3.2 Scanning Electron Microscopy (SEM) with energy dispersive X-ray analysis (EDX)

The characterization of the aluminium alloy samples, after biofouling cleaning, by SEM/EDX, was performed surface and cross-section. The results are summarized in Figures 8 and 9, respectively.

Figure 8a shows the Al-Mg surfaces exposed on light side, which reveal surface morphology modifications linked to the evolution of colonization by microorganisms during immersion time. A cracked surface is observed with the distribution of deposits, drawing the shape of the physiognomy of microorganisms previously present on the surface. The elementary chemical analysis performed by EDX, allowed to verify that there was a magnesium enrichment of the surface.

For the Al-Mg surfaces exposed on dark side (Fig. 8b) a cracked morphology is also observed, being the presence of microorganism colonization significantly less evident. The

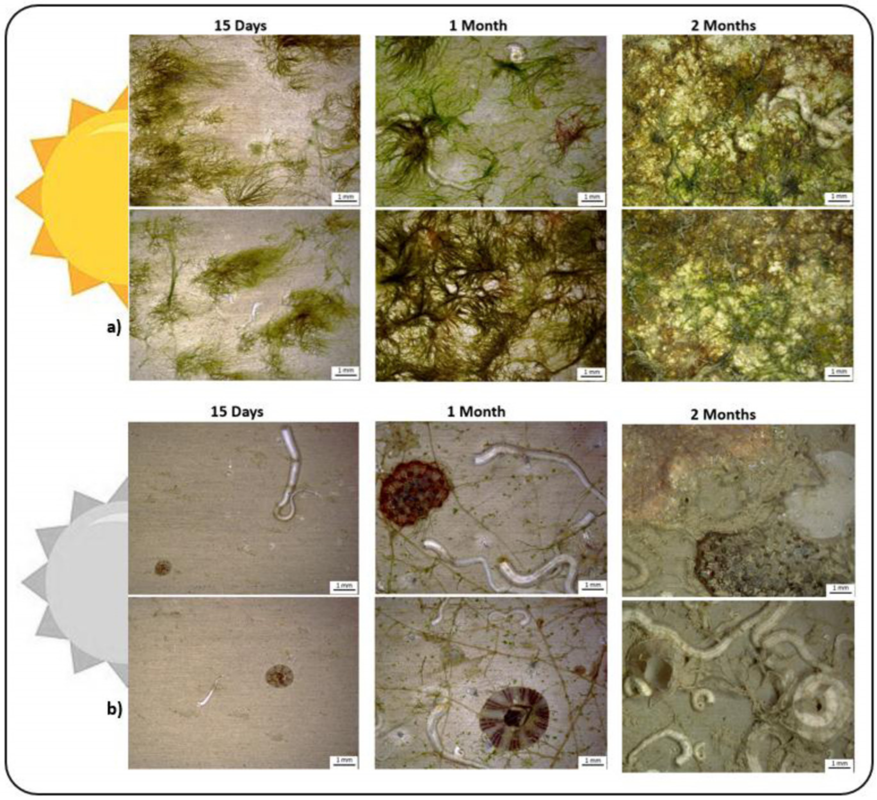

Fig. 6. Digital microscope of Al-Mg samples after 15 days, 1 and 2 months of immersion, light (a) and dark (b) sides of exposure, before biofouling removal.

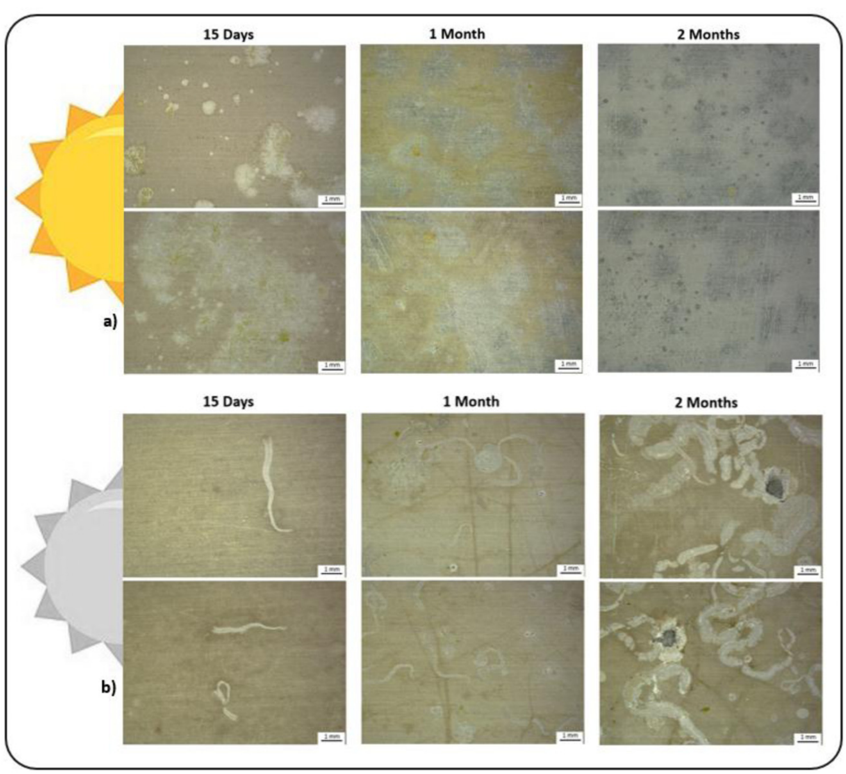

Fig. 7. Digital microscope of Al-Mg samples after 15 days, 1 and 2 months of immersion, light (a) and dark (b) sides of exposure, after biofouling removal.

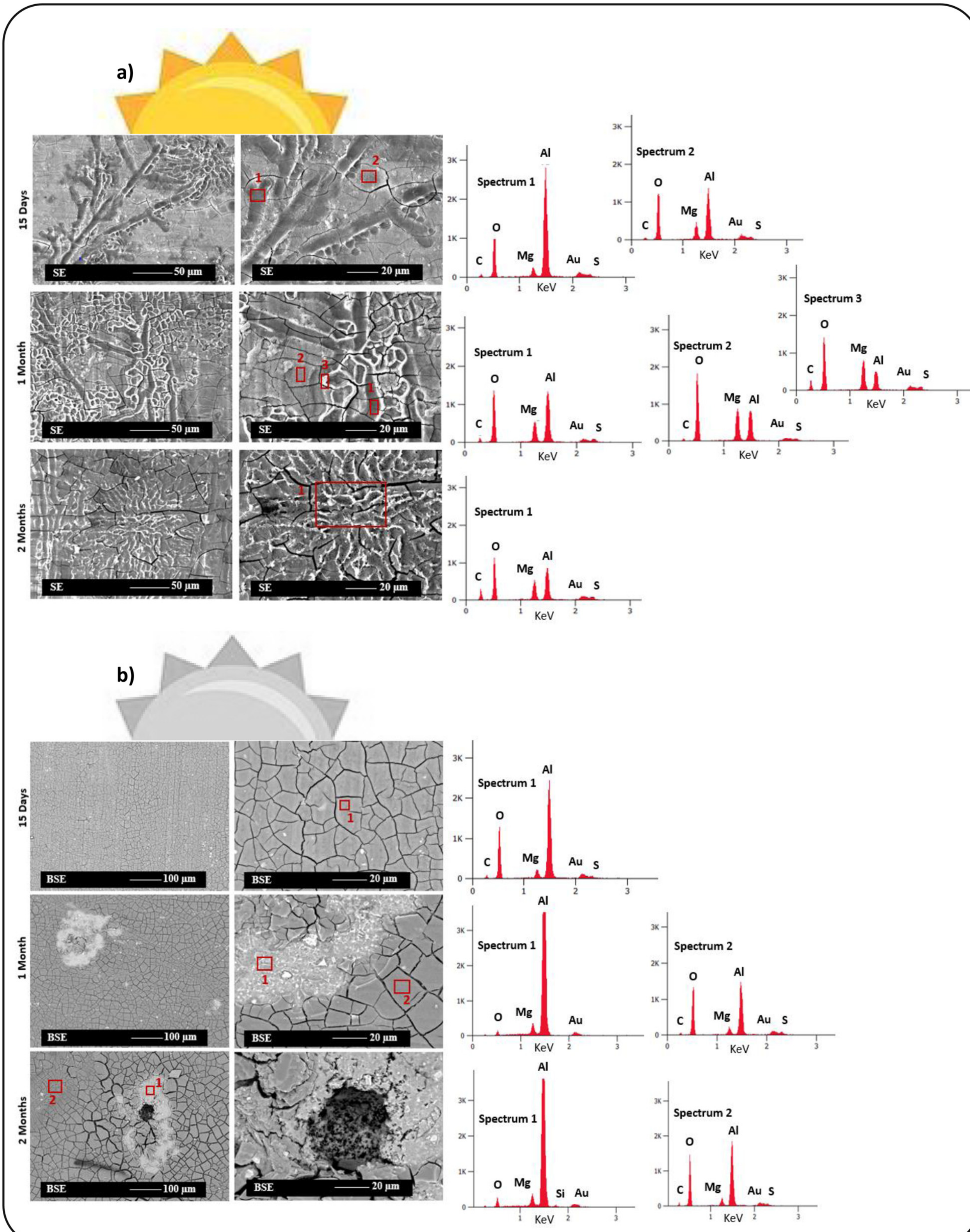

Fig. 8. SEM/EDX characterization of Al-Mg surface immersed for 15 days, 1 and 2 months in seawater (after biofouling removal). (a) Light and (b) dark sides of exposure.

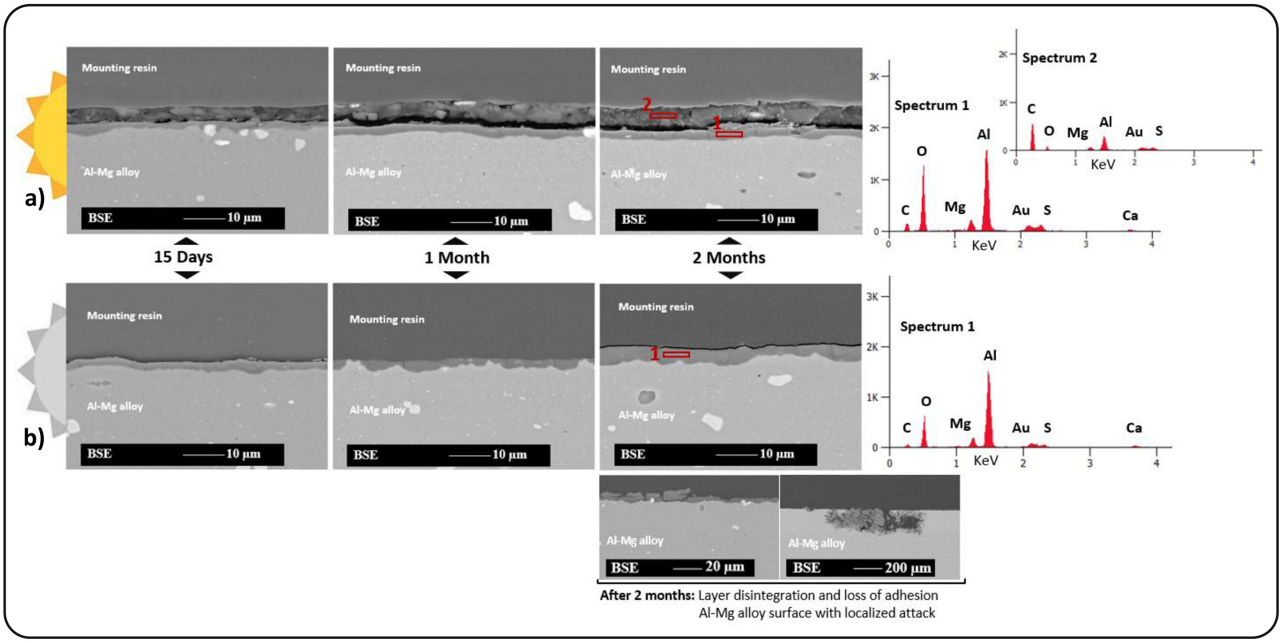

Fig. 9. SEM cross-section characterization of Al-Mg surface immersed for 15 days, 1 and 2 months in seawater (after biofouling removal). (a) Light and (b) dark sides of exposure.

EDX analysis performed identified a lower magnesium enrichment of the surface comparatively to the light side of exposure. After 2 months of immersion pitting corrosion of Al-Mg surface was observed.

Concerning the cross-section characterization, the Figure 9a shows, for the aluminium alloy exposed on the light side, a presence of two distinct layers on the Al-Mg surface. One inner layer with an average thickness in the order of 2 µm, which was found to increase slowly with immersion time, and having an inorganic nature, EDX analysis revealed mainly the presence of aluminium (Al) and oxygen (O), besides magnesium (Mg). The second outer layer had an average thickness between 3,5 µm and 6,5 µm, increasing with time, and was organic-inorganic in nature. In this case, EDX analysis identified a significantly lower presence of aluminium (Al) and a higher presence of carbon (C). No localized attack on the aluminium alloy surface was observed over the immersion time.

On the Figure 9b, related to the exposure of the Al-Mg surfaces on the dark side, the cross-section characterization revealed the presence of only one layer, with an average thickness between 2 µm and 3,5 µm and having an inorganic nature, the EDX analysis revealed mainly the presence of aluminium (Al) and oxygen (O), besides magnesium (Mg). Notwithstanding, the layer increases with immersion time, some disintegration and loss of adhesion are also observed and localized corrosion of the aluminium alloy after 2 months of immersion is also visible.

The schematic representation proposed in Figure 10 summarizes the main points. The initial characterization results of the MICOATEC samples immersed for short time (15 days, 1 and 2 months) in Mediterranean Sea made clear that the type of biofouling developed, according with the side of exposure, light or dark, has a distinct impact on the Al-Mg surface modifications. At the end of 2 months of immersion, no localized corrosion attack was observed on the Al-Mg surface exposed to the light side, contrary to the dark side of exposure, in which localized corrosion attacks were detected. The organic-inorganic layer, only observed on the light side, shows to act as a protective diffusion barrier functioning as potential inhibitor of pitting corrosion in marine environment.

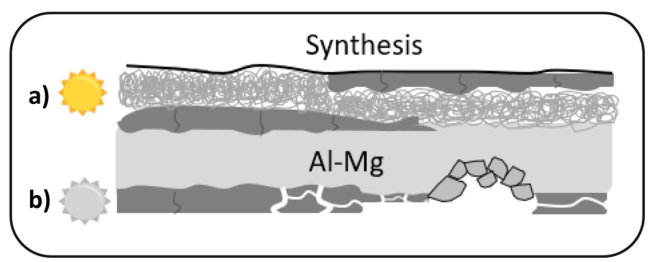

Fig. 10. Schematic representation of the interface AA5083 alloy/seawater, after 2 months of immersion, (a) light and (b) dark sides.

4 Conclusions

The first results of phase 1 of the MICOATEC project have shown that the marine biological activity influences the corrosion behavior of Al-Mg alloy with surface modifications, which can result in a protection effect.

In order to achieve deeper insights into the inhibition corrosion mechanisms on Al-Mg alloy mediated by the microbiological activity in natural seawater, complementary experiments are required. The know-how of MICOATEC project partners allows to have in progress complementary experiments (polarization techniques, microbial analysis and surface advanced analysis techniques, such as XPS, ToF-SIMS and GD-OES) to understand (i) how evolves the Al-Mg surface with longer immersion time in natural seawater, (ii) which main cathodic process is involved, and how it works, and (iii) how the Al-Mg passivity is affected by the biological activity. In particular, it seems important to focus on the specific biological protective processes, which are shown to be associated with direct sunlight exposure.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to this article.

Authors' contributions

All authors have materially participated in the research and the article preparation.

Especially Maria João Marques has performed all the data acquisition and with Régine Basséguy they have performed the conception and design of the study.

All other authors have provided substantial contributions to:
– the analysis and interpretation of the data;
– revising the article draft critically;
– analyzing the literature context and writing the final version.

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