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Corrosion behaviour of the microbially modified surface of 5083 aluminium alloy

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Abstract – The influence of microorganism-induced surface modifications on the corrosion behaviour of 5083 H11 aluminium alloy was studied. Pre-immersion in natural seawater (between 15 days and 2 months) led to the growth of a dense oxy-hydroxyde layer on the AA5083 surface. This layer led to a decrease in the cathodic and corrosion current densities, and an increase in the passivity domain on the polarisation curves plotted in chloride-containing sulphate solution for pre-immersed samples compared to bare samples. This improvement in the corrosion behaviour of AA5083 depended on the alloy microstructure, and the sunlight exposure during the pre-immersion in natural seawater.

Keywords – A. aluminium; A. intermetallics; B. polarization; C. pitting corrosion; C. microbiological corrosion.

1. Introduction

Al-Mg alloys of the 5xxx series are widely used for marine industry because of their high corrosion resistance, lightness and excellent processing performance [1–4]. However, they still remain susceptible to pitting and intergranular corrosion (IGC) when exposed to chloride media, despite the spontaneous formation of a thin protective oxide film on their surface [2,5–8]. It is therefore necessary to improve their corrosion resistance, and several strategies can be used. From a global point of view, conversion coatings can be considered as one of the most successful and cost-effective alternatives to efficiently increase the corrosion resistance of these metals and abundant literature exists on this topic [9–14]. However, towards a more constraining legislation as REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals), the surface treatment industry looks for more innovative and environmentally friendly alternatives and nothing is greener than Nature, which inspires new concepts to improve corrosion resistance performance.

Natural seawater is a complex corrosive medium composed of salts, dissolved gases and organic matter related to living organisms. The presence of microorganisms may cause either corrosion acceleration or inhibition, processes known as Microbiologically Influenced Corrosion (MIC) or Microbiologically Influenced Corrosion inhibition (MICI), respectively [15–19]. MIC in seawater has been largely studied for stainless steels, and the ennoblement of the open circuit potential (OCP) observed in all seawaters was proved to be the consequence of the biofilm formation [20]. Indeed, Scotto *et al.* followed the OCP of stainless steel during immersion in seawater in Genoa Harbour, and showed that the introduction of sodium azide (NaN_3), a chemical that destroyed microorganisms, stopped the ennoblement process (OCP drops down) [21]. To explain the OCP ennoblement that increases the risks of pitting corrosion, the most

proposed mechanism is the catalysis of oxygen reduction reaction caused by the biofilm [22]. MICI process has also been studied for steels in presence of marine bacteria [23–25]. The microorganisms that adhere to the surface of steels can promote a bio-mineralisation process: the layer formed can provide a barrier against corrosive media and inhibits corrosion.

Contrary to steels, only few studies of MIC/MICI in marine environment can be found for Al alloys. Some of them are carried out in natural seawater [26,27], and some in laboratory [28–30]. Guan et *al.* found that sulphate-reducing bacteria (SRB) could accelerate the uniform and localised corrosion of 5052 Al alloy leading to surface modification due to SRB biofilm formation on the sample surface [31]. On the contrary, Shen et *al.* studied the impact of *Bacillus subtilis* on the corrosion processes of Al alloy 2A14, and showed that the corrosion rate was strongly reduced in the presence of microorganisms [32]. This short review showed that the corrosion behaviour of Al alloys in the presence of marine microorganisms depends on the type of microorganisms, some inhibiting the corrosion processes, whereas others lead to an acceleration of the damage. However, few works have studied the impact of bio-mineralization on Al alloy. Marques et *al.* studied the surface of 5083 H11 Al alloy samples after a two-year exposure in natural seawater [26]. They showed that a layer formed in the immersed zone and inhibited corrosion, whereas the non-immersed zone was covered by pits. In the same way, Jaume et *al.* studied the influence of the marine microbial population on the corrosion behaviour of AA5083 H11 specimen [33]. They showed that the microbial activity led to the formation of a double-structure layer: a dense, amorphous inner layer and a more porous outer layer on the Al surface, which ultimately protected it against further corrosion. These latter results suggested that it could be interesting to exploit the surface modifications due to exposure to the marine environment as a protective treatment against corrosion.

In this framework, the aim of the present work is to analyse how surface modifications, induced by a pre-immersion in natural marine environment of an AA5083 Al-Mg alloy, impact the subsequent corrosion behaviour of the alloy. This study was carried out on two Al-Mg alloy sheets of the same grade, but of different thicknesses associated with differences in microstructure. The surface modifications of the alloy after different immersion times in natural seawater were observed using scanning electron microscopy (SEM). The composition of the layer formed on the alloy surface was investigated by energy dispersive spectroscopy (EDS) and Glow Discharge Optical Emission Spectroscopy (GDOES). Then, polarisation tests were carried out on pre-immersed samples to further analyse the protective effect of the layer formed on the alloy surface. The mechanisms of layer formation and growth during pre-immersion in natural seawater were not the focus of the present study; in particular, understanding the action of the microorganisms on layer growth was not the focus of the study. However, control tests were also performed with samples pre-immersed in sterilised seawater to clearly demonstrate that the improvement in corrosion resistance resulted from exposure to seawater under biotic conditions.

2. Materials and methods

2.1. Materials

The material studied is an Al-Mg 5083 H11 alloy. It was provided as hot-rolled plates with two thicknesses: 1 mm and 7 mm. The weight percentage of alloying elements is shown in Table 1. Some slight differences are observed between the 7 mm plate and the 1 mm plate, with higher Mg, Fe and Si amounts for the 7 mm plate.

The corrosion behaviour of the plates (100 x 200 mm² rectangles in the rolling plane) was studied in the as-received state (samples referred to as bare samples), and after pre-immersion in natural Genoa seawater (biotic conditions, samples referred to as samples pre-immersed in

Genoa seawater). Some experiments were also performed with samples pre-immersed in sterilised seawater (abiotic conditions, samples referred to as samples pre-immersed in sterilised seawater) for comparison. Prior to pre-immersion (in sterilised and Genoa seawater), the as-received plates were cleaned with 99% purity ethanol. For samples pre-immersed in sterilised seawater, the as-received plates were immersed vertically for 1 month in a closed container containing 6 L of sterilised seawater. The seawater was collected near the coast at Gruissan (France), and was sterilised through a 0.2 μm filter. An air bubbling system was installed to ensure constant oxygenation and to create agitation similar to that in real conditions, but without microorganisms. After pre-immersion in sterilised seawater, the samples were washed with tap water and then distilled water with a vegetable sponge before being stored in airtight boxes with silica gel. For samples pre-immersed in Genoa seawater, the as-received plates were immersed vertically in seawater at the Genoa Experimental Marine Station (GEMS) - CNR-IAS for different periods of time: 15 days, 1 month, and 2 months from September to November. In this configuration, where the plate is immersed vertically, one side of the plate is exposed to the direct light of the sun and the other one faces the shadow: the sides are called light side and dark side, respectively. The seawater temperature, salinity, conductivity and pH were recorded once a week; the mean values were 22.1 ± 2.4 °C for temperature, 37.5 ± 0.9 ‰ for salinity, 54 ± 4 mS cm^{-1} for conductivity, and 8.1 ± 0.1 for pH. After pre-immersion in Genoa seawater, the samples were rinsed with tap water, then air-dried and wrapped in absorbent paper before being stored in airtight boxes with silica gel and sent to our laboratory. Prior to use, they were washed in tap and then distilled water with a vegetable sponge and a spatula to remove the macrofouling on the sample surface. They were then rinsed with distilled water and dried in hot air. They were again stored in airtight boxes with silica gel until used for testing. The first laboratory tests started about 2 months after the pre-immersion stage was completed.

In the following, for both bare and samples pre-immersed in Genoa seawater, different planes were studied: the rolling plane for 1 mm and 7 mm plates, and a transverse plane for the 7 mm plate only, referred to as 1 mm L-LT, 7 mm L-LT and 7 mm LT-ST, respectively, where L, LT and ST are the rolling, long transverse and short transverse directions, respectively. For samples pre-immersed in sterilised seawater, only the rolling plane of the 1 mm plate was studied. It was assumed that this set of experiments was sufficient to assess the effect of microorganisms on surface changes during pre-immersion in natural seawater. Test specimens with a cylindrical shape (disc with a 45-mm diameter in the rolling plane) for 7 mm and 1 mm L-LT, and parallelepipeds (20 x 7 mm² rectangular surface in the LT-ST plane) for the 7 mm LT-ST plane were machined from the plates. For the samples pre-immersed in Genoa seawater, specific attention was paid to the surface during machining in order not to damage the microbially-modified surface. The same precautions were taken for the samples pre-immersed in sterilised seawater.

2.2. Analysis of the microstructure of AA5083 alloy

To identify the type, the global distribution and the morphology of coarse intermetallic particles (IMCs) of AA5083 Al alloy, bare samples were mounted in an epoxy resin, ground using SiC abrasive paper down to 2400, then polished with diamond paste down to 1 µm and finally using a colloidal silica (OPS). An optical microscope (OM, MA200 Nikon) and a Scanning Electron Microscope (SEM, FEI Quanta450) coupled with Energy Dispersive X-ray Spectroscopy (EDS Bruker) were used to characterise IMCs. For each sample, approximately 25 optical images were analysed using ImageJ software. A cumulative average of the fraction of surface area covered by IMCs was calculated.

The grain structure was analysed using OM. Before observations, samples were polished as before, then electrolytically etched with a 3.5% vol. HBF₄ reagent.

2.3. Characterisation of the samples pre-immersed in Genoa seawater and in sterilised seawater

A SEM (FEI Quanta450) coupled with EDS (EDS Bruker) was used to analyse the surface of the samples pre-immersed in Genoa seawater and in sterilised seawater, and to determine the thickness of the layer formed during pre-immersion. For the latter, observations were made using cross-section samples polished following the procedure used for the analysis of IMCs.

In addition, in order to identify the composition of the layer, EDS mapping on cross-sections (SEM/FIB FEI HELIOS 600i coupled with EDS, Raimond Castaing Microanalysis Center, Toulouse, France) and Glow Discharge Optical Emission Spectroscopy analyses (GDOES GD-profiler 2 of the brand Horiba, Raimond Castaing Microanalysis Center, Toulouse, France) were performed. The GDOES depth profiles were performed at 30 W and 650 Pa.

2.4. Electrochemical behaviour of bare samples, samples pre-immersed in Genoa seawater and samples pre-immersed in sterilised seawater

Prior to any electrochemical tests, bare samples were ground with SiC paper down to 240. Concerning the samples pre-immersed in Genoa seawater and in sterilised seawater, no specified preparation was made before electrochemical tests, except for the washing step described in section 2.1.

The corrosion behaviour was studied by plotting polarisation curves in a 0.001 M NaCl + 0.1 M Na₂SO₄ solution using a three-electrode cell. In the present study, our objective was to evaluate the electrochemical response of samples covered with the layer formed during pre-immersion in natural seawater: for this purpose, an electrolyte of moderate aggressiveness had to

be chosen. The durability of this layer could have been tested in a common 3.5 % NaCl solution. However, such an aggressive electrolyte would have masked interesting data regarding the electrochemical response of bare specimens compared to samples pre-immersed in Genoa seawater with a modified surface. An Ag/AgCl/KCl (saturated) electrode and a platinum foil were used as reference and counter electrodes, respectively. Nevertheless, for easy comparison with literature data, in the following, all potentials are quoted in relation to the saturated calomel electrode (SCE). Samples were vertically positioned in the electrochemical cell; as indicated before, for the 1 mm and 7 mm L-LT samples, the surface exposed to the electrolyte was a 45-mm disc, whereas, for the 7 mm LT-ST sample, it was a 7 x 20 mm² rectangle. Due to their shape and/or thickness, 7 mm LT-ST and 1 mm L-LT samples were mounted into an epoxy resin with a Cu wire for electrical connection, before electrochemical tests. Before polarisation tests, the samples were immersed at their open circuit potential (OCP) for 30 minutes to figure out a near stationary state. The polarisation curves were plotted at a scanning rate of 0.139 mV/s from OCP + 20mV to OCP – 1000 mV for the cathodic curves, and from OCP - 20mV to a potential corresponding to a current density of 1 mA cm⁻² for the anodic curves. Each test was reproduced at least two times for reproducibility. After the electrochemical measurements, surface analyses were conducted by using OM (MA200 Nikon) and SEM (FEI Quanta450).

Furthermore, pit propagation was studied in the same electrolyte, i.e. in a 0.001 M NaCl + 0.1 M Na₂SO₄ solution: samples were maintained at OCP for 5min or 24 hours, then polarised in the anodic domain at a fixed current density of 0.1 mA cm⁻² for 10 min to have a similar charge passed through all samples. The pit size and density were determined by using a confocal microscope (Sensofar S Neox), and Electron Backscatter Diffraction (EBSD, Oxford Instruments HKL EBSD System mounted on a Field-Emission Gun (FEG) SEM JEOL JSM 7100 F) was used to characterise pit propagation.

3. Results and discussion

3.1. Study of the microstructure of AA5083 H11 Al alloy

Firstly, the IMCs present in the different samples of AA5083 H11 alloy were observed by OM (Fig. 1). Two types of IMCs were observed on the surface having a dark and a light grey appearance. EDS analyses were performed for IMC identification: the dark particles were identified as Mg-rich particles, containing also Si, and the light grey were identified as Fe-rich particles, corresponding to Al-Fe-Mn phases. The composition of these IMCs is in agreement with that observed for the same alloy by various other authors [34,35] who have reported that these phases are likely $\text{Al}_6(\text{Mn,Fe})$ and Mg_2Si . The fraction of surface area covered by the particles was also determined (Fig. 2). For the 7 mm LT-ST samples, the analysis was performed both at the surface (referred to as skin, near the L-LT plane) and in the core of the plate. For all samples, Al-Fe-Mn particles were found to be more abundant than Mg-rich particles. Moreover, whatever the particles, a higher fraction of surface area covered by the particles was determined for the 7 mm plate by comparison to the 1 mm plate, which is in agreement with the chemical composition of the two plates. Regarding the 7 mm plate, differences were observed depending on the plane, with more particles in the LT-ST plane compared to the rolling plane (L-LT).

Fig. 1 (e) to (h) show OM images of the grain morphology after chemical etching. Similar microstructures were observed for the rolling planes of 1 mm L-LT and 7 mm L-LT samples with recrystallised structure and equiaxed grains of $28 \pm 2 \mu\text{m}$ and $31 \pm 1 \mu\text{m}$ in diameter for the 1 mm L-LT and 7 mm L-LT samples, respectively (Fig. 1 (e) and (f)). For the 7 mm LT-ST sample, results show a gradient in microstructure in the ST direction which is related to rolling. Near the surface of the plate (Fig. 1 (h)), a recrystallised structure with grains of $29 \pm 6 \mu\text{m}$ was

observed similarly to the 7 mm L-LT sample, whereas, in the core of the plate, the microstructure is characterised by grains elongated in the LT direction with an average length of $35 \pm 13 \mu\text{m}$ (Fig. 1 (g)). Panagopoulos *et al.* [36] observed these heterogeneities in grain size for a 5083 Al alloy and showed a slight decrease in grain size when the rolling rate of the plate (initial thickness of 3 mm) was increased from 7 % to 15 % leading to a final thickness of 2.8 mm and 2.5 mm, respectively. She *et al.* [37] also observed microstructural differences in the LT-ST plane of a 105 mm thick plate of 5083 Al alloy when they performed grain size measurements between 20 and 30 mm far from the surface (L-LT plane).

The results thus showed differences in the microstructure between the 1 mm and the 7 mm plates, and differences between the different planes of the 7 mm plate. Therefore, it was relevant to determine whether those differences could have a significant influence on the behaviour of the samples during pre-immersion in seawater and on their resulting corrosion behaviour.

3.2. Characterisation of the modified surfaces after pre-immersion in Genoa seawater and sterilised seawater

Fig. 3 shows OM images of the 1 mm L-LT sample surface before (bare sample, Fig. 3 (a)) and after pre-immersion in Genoa seawater for 15 days (Fig. 3 (c) and (f)), 1 month (Fig. 3 (d) and (g)) and 2 months (Fig. 3 (e) and (h)). Similar observations were obtained for 7 mm L-LT and LT-ST samples, but the results are not given for brevity. For all samples, first visual observations showed differences between the surfaces of bare samples and samples pre-immersed in Genoa seawater.

The modifications occurring on the sample surface during pre-immersion in Genoa seawater were associated with the growth of a layer that could be observed from 15 days of exposure (Fig.

4). For all samples, the layer was found inhomogeneous for both the light and dark sides, but this was more true for the dark side. Furthermore, when the duration of pre-immersion in Genoa seawater was increased, the layer was more homogeneous for both dark and light sides. However, a few pits were observed after 2 months of pre-immersion in Genoa seawater for the dark side (arrows in Fig. 3 (h)). An OM image of the surface of the 1 mm L-LT sample after a one-month pre-immersion in sterilised seawater is also given for comparison in Figure 3 (b). A layer was also observed on the sample surface, but first visual inspection suggested that this layer was thinner than after a one-month pre-immersion in Genoa seawater. In addition, the sample surface was covered with numerous pits, suggesting that the layer formed in sterilised seawater was less protective than that formed in Genoa seawater for the same pre-immersion time.

To go further in the characterisation of the modified surfaces, the composition of the layers formed during pre-immersion in Genoa seawater was determined. The distribution of the main chemical elements detected in the layers was analysed by plotting, from the layer to the substrate, SEM EDS maps using cross-section samples (Fig. 4), and GDOES profiles (Figs. 5, 6 and 7). For example, Fig. 4 shows the results obtained for the layer formed on the light side of the 1 mm L-LT sample (Fig. 4 (a) to (d)) and the 7 mm L-LT sample (Fig. 4 (e) to (h)) after 15 days of pre-immersion in Genoa seawater. Similar conclusions are obtained for the light side of the other samples and for the dark side of all the samples. The layer was cracked, which could be due to vacuum in SEM, but seemed to be adherent with the substrate (Figs. 4 (a) and (e)). It was found to contain mainly O, Al and Mg, with a homogeneous distribution of O and Al inside the layer (Figs. 4 (b) and (c) for 1 mm L-LT sample, and 4 (f) and (g) for 7 mm L-LT sample), whereas Mg was mainly present in a thin film on the external part of the layer (Figs. 4 (d) and (h) for 1 mm and 7 mm samples, respectively).

GDOES profiles plotted for the light side of samples pre-immersed in Genoa seawater (Figs. 5, 6 and 7) confirmed these results. Considering first the results obtained for the 7 mm L-LT sample pre-immersed for 15 days in Genoa seawater (Figs. 5 and 6), for the Al signal, from the sample surface to the substrate, a plateau corresponding to a low amount of Al was first observed, followed by an increase in the Al signal after 2 μm of sputtering depth before stabilisation at a higher amount of Al after 3.5 μm of sputtering depth. In parallel, for the O signal, a plateau showing a high amount of O was observed for [0 – 2] μm of sputtering depth, followed by a decrease in the O signal and a stabilisation at a lower intensity after 3 μm of sputtering depth. The analysis of the signals corresponding to these 2 elements led to identify 3 different areas: a first area identified as the layer formed during pre-immersion, a second area named interfacial zone, and a third area which corresponded to the substrate. It was not possible to distinguish between the layer formed during pre-immersion and the interfacial zone on SEM images. GDOES profiles also showed the presence of H inside the layer with H enrichment at the extreme surface as well as in the interfacial zone. The results thus showed that the layer was an Al oxy-hydroxide with a Mg enrichment at the extreme surface probably linked to the formation of a Mg oxide or hydroxide, in agreement with the SEM EDS maps described above (Fig. 4). Other elements were also detected during GDOES analyses, i.e. Ca and S, with Ca enrichment in the interfacial zone and S enrichment both in the extreme surface and in the interfacial zone.

Fig. 5 also shows GDOES profiles plotted for the 7 mm L-LT sample after 1 month and 2 months of pre-immersion in Genoa seawater, which allows to determine the influence of the pre-immersion duration time on the composition and thickness of the layer formed during pre-immersion. The same elements were detected, and the global shape of the profiles for all the elements was similar whatever the pre-immersion time in Genoa seawater, so that the layer

formed during pre-immersion, an interfacial zone and the substrate were identified for all profiles as previously done. However, the abrupt increase in the Al signal was shifted from 2 to 2.4 and 2.7 μm of sputtering depth, and the plateau corresponding to high Al amount was reached after 3.5, 4.5 and 5 μm for layers formed after 15 days, 1 month and 2 months, respectively. In parallel, the abrupt decrease in O signal was shifted from 2 to 2.4 and 2.7 μm of sputtering depth for layers formed after 15 days, 1 month and 2 months, respectively, whereas the intensity of the O signal on the first plateau increased when the duration time of pre-immersion increased. The results thus showed a thickening of the layer when the duration time of pre-immersion in Genoa seawater was increased. Moreover, it was of interest to note the significant O enrichment at the extreme surface after 1 and 2 months. This could be related to the Mg enrichment at the extreme surface of the layer formed during pre-immersion, which was also found to increase when the layer thickened. The shift of the GDOES profiles was also observed for the other elements; moreover, the intensity of the S, H and Ca peaks in the interfacial zone increased when the pre-immersion duration time was increased. All the observations strengthened the conclusion that the thickness of the layer increased when the duration of pre-immersion in Genoa seawater was increased.

Then, the results obtained for the 7 mm L-LT sample were compared with those obtained for the 1 mm L-LT sample. Mg GDOES profiles plotted for the 1 mm L-LT sample was added in an insert in Fig. 5 (Mg signal). Comparison with the Mg profiles plotted for the 7 mm L-LT sample showed not only that the Mg amount in the extreme surface was lower, but also that the Mg enrichment occurred for longer time of pre-immersion (1 month) for 1 mm L-LT sample compared to 7 mm L-LT sample. This result was consistent with the composition of the 2 plates (Table 1, lower Mg content in 1 mm sample) and showed an influence of the alloy microstructure on layer growth during pre-immersion in Genoa seawater. To go further in the

analysis of the influence of the alloy microstructure on the thickness and composition of the layer formed during pre-immersion, GDOES profiles of the other elements were also plotted for the 1 mm L-LT sample. Results are given after 15 days of pre-immersion in Genoa seawater in Figure 6. They allowed to distinguish between the layer formed during pre-immersion, an interfacial zone and the substrate for the 1 mm L-LT sample as for the 7 mm L-LT sample. However, as previously noted for the Mg signal, results showed that the amounts of S and H were globally more important in the layer formed on the 7mm L-LT sample than on the 1 mm L-LT sample. Furthermore, the analysis of all the signals, except this of O, suggested that the layer was thicker on the 7 mm sample than on the 1 mm sample. When the pre-immersion in Genoa seawater was longer, i.e. 1 month (Fig. 7), a thickening of the layer formed on the 1 mm L-LT sample compared to the sample pre-immersed for 15 days (Fig. 6) was observed, as it was for the 7 mm L-LT sample. It was also interesting to note that, after 1 month of pre-immersion in Genoa seawater, the abrupt variations of the Al and O signals were observed for similar sputtering depths for the 1 mm and 7 mm samples, suggesting that, for this pre-immersion duration time, the layers formed on the 1 mm L-LT and 7 mm L-LT samples had a similar thickness. However, as observed in Fig. 4, the heterogeneity of the layer thickness could not be neglected. Therefore, a statistical analysis of the layer thickness had to be performed to strengthen the conclusions (see comments on Fig. 8 below).

Analyses were also performed for the 7 mm LT-ST samples: globally, the results were similar to those observed for the 7 mm L-LT samples. They are not given for brevity.

The results described above for the samples after pre-immersion in Genoa seawater were in accordance with other studies [33,38]. Jaume et al. [33] observed a double-structure layer for the same AA 5083 Al-Mg alloy pre-immersed in natural seawater with salt marsh used as a source

of microorganisms: a dense and amorphous internal layer rich in O, Si and Ca and a porous external layer rich in Mg. Shen et al. [32] showed the formation of a protective layer of $\text{CaMg}(\text{CO}_3)_2$ on 2A14 Al alloy in seawater in presence of the bacteria *B. subtilis*: the formation of this chemical compound could be due to interactions of microbial activities and seawater containing Ca and Mg ions. Other authors have also observed the formation of an organic-inorganic hybrid film composed of organic matter (characterised by C-H and O-H bond peaks) and calcite ($(\text{Mg}_{0.064}\text{Ca}_{0.936})\text{CO}_3$) on steel after 14 days of immersion in marine broth medium containing different strains of bacteria *Pseudoalteromonas lipolytica* [24]. Moreover, Dupraz et al. [39] also showed the precipitation of CaCO_3 due to the activity of microorganisms, producing CO_2 at concentrations allowing the formation of CaCO_3 . In addition, the presence of S in our samples after pre-immersion in Genoa seawater could also be due to the metabolic activity of a specific microorganism SRB, which is conventionally attributed to the corrosiveness of H_2S [40]. However, our analyses did not distinguish between sulphate and sulphide species; therefore, the detection of S could also result solely from the incorporation of sulphate from Genoa seawater.

To support the above explanations, and although the mechanisms of layer growth during pre-immersion in Genoa seawater and the influence of microorganisms on this process were not the scope of this study, GDOES profiles were also plotted for the 1 mm L-LT sample after 1 month of pre-immersion in sterilised seawater for comparison (Fig. 7). Overall, the same elements (Al, O, S, H, Ca and Mg) were detected. The Al and O signals showed a global shape similar to that observed for the samples pre-immersed in Genoa seawater, which allowed the layer, an interfacial zone and the substrate to be distinguished. The H enrichment at the sample surface showed that the layer formed in sterilised seawater was also an oxy-hydroxide layer. However, the abrupt increase in the Al signal and abrupt decrease in O signal occurred after only 1 μm of

sputtering depth for the sample pre-immersed for 1 month in sterilised seawater compared to 2.5 μm for the 1 mm L-LT sample pre-immersed for 1 month in Genoa seawater: this showed that the layer formed in sterilised seawater was significantly thinner than that formed during pre-immersion in Genoa seawater.

In addition, the layer formed in sterilised seawater also contained S, but, in this case, this could not be attributed to the activity of microorganisms. This result therefore showed that S, probably from sulphate ions contained in sterilised seawater, could be incorporated into the layer during its growth. This suggested, as mentioned earlier, that the amount of S detected for the sample pre-immersed in Genoa seawater was probably related, at least in part, to S incorporated as sulphate ions from Genoa seawater. However, the presence of S in the form of sulphide ions in the layer formed in Genoa seawater, due to the activity of microorganisms could not be excluded; this hypothesis was strengthened by the higher amount of S in the layer formed in Genoa seawater compared to that formed in sterilised seawater. Similarly, the amount of Ca was significantly lower in the layer formed in sterilised seawater compared to that formed in Genoa seawater. Again, this could be explained by considering that, for the sample immersed in sterilised seawater, the amount of Ca was only related to the presence of Ca species in the seawater, Ca being simply incorporated into the layer during its growth. On the contrary, the high amount of Ca in the layer formed on the sample pre-immersed in Genoa seawater suggested that Ca was incorporated into the layer from the Ca species present in seawater, but its presence inside the layer was also the result of the activity of the microorganisms. Finally, it was also important to note the very high amount of Mg within the layer formed in sterilised seawater, whereas Mg was only found to be segregated at the extreme surface for the samples pre-immersed in Genoa seawater. The result confirmed that the sample was much more reactive in

the absence of microorganisms, and that the layer formed was significantly less protective than that formed in Genoa seawater.

In order to obtain consolidated data concerning the thickness of the layer formed during pre-immersion, this structural parameter was determined by SEM observations carried out on cross-sections prepared for the samples pre-immersed in Genoa seawater and sterilised seawater. The results are given in Fig. 8 for the light and dark sides of 1 mm L-LT, 7 mm L-LT and 7 mm LT-ST samples after 15 days, 1 month and 2 months of pre-immersion in Genoa seawater. For comparison, the results were also presented for the 1 mm L-LT sample pre-immersed for 1 month in sterilised seawater. For each condition, e.g. the 1 mm L-LT sample pre-immersed in Genoa seawater for 1 month, measurements were made on two specimens prepared at the same time with exactly the same procedure. For each specimen, the thickness of the layer was measured over a length of about 1.4 cm, which corresponded to about 20 measurements per specimen. This means that, for each condition, 40 measurements were made. This statistical analysis is illustrated by a boxplot representation. Considering that the layer thickness was not homogeneous (Fig. 3), this led to a large dispersion on the values given in Figure 8. However, given this statistical analysis of the thickness, we assumed that the average values obtained for thickness were relevant.

First, concerning the light side, Fig. 8 (a) showed that a thicker layer formed on the 7 mm plate compared to the 1 mm plate regardless of the pre-immersion duration time, which confirmed the previous results (Fig. 6). Furthermore, for the 7mm plates, differences in the layer thickness were observed between the both L-LT and LT-ST planes. Indeed, for long pre-immersion times, i.e. after 1 and 2 months of immersion, the layer was thicker on the 7 mm LT-ST plane than the 7 mm L-LT plane. An influence of the sunlight exposure (direct or shadow) on

the growth of the layer was observed, with in particular a stronger scattering in the thickness values for the dark side compared to the light side, in agreement with previous OM observations (Fig. 3). However, globally, even for the dark side, the layer was thicker for the 7 mm LT-ST samples compared to both 1 mm L-LT and 7 mm L-LT samples, for the longest pre-immersion times. Finally, statistical analysis of the layer thickness confirmed that the layer formed in sterilised seawater was significantly thinner than that formed in Genoa seawater, as previously shown by the GDOES profiles (Fig. 7).

3.3. Corrosion resistance of the samples pre-immersed in Genoa seawater and in sterilised seawater

Current-potential curves plotted in chloride-containing sulphate solution for the samples pre-immersed in Genoa seawater are presented in Figs. 9 and 10 for the light and dark sides, respectively. The curves plotted for the bare samples and for the 1 mm L-LT sample pre-immersed for 1 month in sterilised seawater are also shown for comparison.

For all bare samples, the cathodic curves presented a globally similar shape; the main cathodic reaction, at least for potentials between the corrosion potential E_{corr} and $E_{\text{corr}} - 200$ mV, corresponded to the reduction reaction of dissolved oxygen. The anodic curves showed a passivity plateau followed by a sharp increase in the anodic current densities. This reflected corrosion kinetics controlled by the properties of the passive film. However, since the current measured in the passive region is a function of the scan rate and will only approach the corrosion current for an infinitesimally slow scan rate, the corrosion current density, J_{corr} , was calculated by extrapolating the cathodic currents in Tafel plots (Fig. 9 and 10).

OM observations (not shown) performed after the potentiodynamic polarisation tests in the cathodic domain showed dissolution phenomena around Al-Fe-Mn IMCs due to oxygen reduction at these sites, in agreement with literature showing that the cathodic reactions take place preferentially on those particles which are more noble than the surrounding matrix [41–43]. After polarisation in the anodic domain, numerous pits were observed on the sample surface, which evidenced that the passivity breakdown was related to pitting corrosion. Therefore, the breakdown potential observed in the anodic domain was referred to as E_{pit} , and the width of the passivity plateau, referred to as ΔE where $\Delta E = E_{\text{pit}} - E_{\text{corr}}$, was representative of the resistance to pitting corrosion of the sample. Due to their nobility, the Al-Fe-Mn particles were preferential pit initiation sites with, as said previously, dissolution of the surrounding matrix.

Characteristic values of J_{corr} , J_{cath} , E_{corr} and ΔE are reported in Fig. 11. For all bare samples (dark grey bars), E_{corr} values were similar and varied between - 0.71 and - 0.75 V_{SCE} . J_{cath} values correspond to the cathodic current densities measured at a potential equal to $E_{\text{corr}} - 120$ mV. Higher J_{cath} values were measured for the 7 mm L-LT and 7 mm LT-ST samples compared to the 1 mm L-LT sample. This was in agreement with the higher fraction of surface area covered by Al-Fe-Mn IMCs in the 7 mm samples compared to the 1 mm L-LT sample (Fig. 2). Moreover, despite the large standard deviation observed, J_{corr} values were significantly higher for the 7 mm samples compared to the 1 mm sample, which was also in agreement with the higher density of IMCs in the 7 mm samples (Fig. 2), those particles promoting the destabilisation of the passive film. Surprisingly, this did not lead to significant variation in E_{pit} , and thus ΔE values. Nevertheless, considering J_{corr} values, it could be concluded that the 7 mm samples had a lower corrosion resistance than the 1 mm L-LT sample, which was correlated with higher fraction of surface area covered by IMCs.

For the samples pre-immersed in Genoa seawater, current-potential curves plotted (Fig. 9 and 10) were similar to those of the bare samples, indicating that the presence of the layer formed during the pre-immersion in Genoa seawater did not change significantly the cathodic and anodic processes that occurred during the polarisation in the chloride-containing sulphate solution. Therefore, the same electrochemical parameters were extracted from the current-potential curves for the samples pre-immersed in Genoa seawater (Fig. 11).

First, attention was paid to the light side for which the layer formed during pre-immersion was previously observed as being more homogeneous than that formed on the dark side. Results showed that no clear tendency was noted concerning E_{corr} values for all the samples pre-immersed in Genoa seawater compared to the corresponding bare samples. However, for the samples pre-immersed in Genoa seawater, the current densities were lower compared to the bare samples, both in the cathodic and anodic domains. Indeed, the samples pre-immersed in Genoa seawater were associated with significantly lower J_{cath} values compared to the corresponding bare samples, for both 1 mm and 7 mm samples, and whatever the duration time of pre-immersion in seawater. Globally, the pre-immersed 1 mm L-LT samples showed the lowest J_{cath} values, whereas the pre-immersed 7 mm LT-ST samples had higher J_{cath} values compared to both the pre-immersed 1 mm L-LT and 7 mm L-LT samples. Moreover, lower J_{corr} values were measured for all the samples pre-immersed in Genoa seawater compared to the corresponding bare samples. Finally, for all the samples pre-immersed in Genoa seawater (except for the 7 mm L-LT sample pre-immersed for 2 months), higher ΔE values associated with an extended passivation domain were calculated whatever the pre-immersion duration time compared to the corresponding bare samples. Therefore, the results showed that the layer formed during the pre-immersion in Genoa seawater could be considered as an efficient protection against corrosion for the AA5083 samples, for both 1 mm and 7 mm samples. No clear tendency was observed concerning the influence of the pre-immersion duration time on the

electrochemical parameters values, but this was assumed to be related to the lack of homogeneity of the layer formed during pre-immersion. Besides, when attention was paid to the dark sides, it could be observed that globally similar conclusions as for the light side could be drawn. From a global point of view, the standard deviation calculated for each parameter, i.e. E_{corr} , ΔE , J_{corr} and J_{cath} , was quite high for the samples pre-immersed in Genoa seawater. This might be a marker of the strong heterogeneity of the layer which could be explained by referring to the heterogeneity of the microstructure of the substrate, i.e. AA5083, with probably a significant influence of microstructural features of the substrate on the local properties of the layer formed during pre-immersion. Therefore, it was quite difficult to deduce, from the current-potential curves, a significant influence of lightness or microstructure on the protection efficiency of the layer formed during pre-immersion. However, as indicated previously, the comparison between bare and samples pre-immersed in Genoa seawater clearly indicated the positive role of the layer formed during pre-immersion on the corrosion behaviour of AA5083, for both 1 mm and 7 mm samples.

In addition, the results showed that the J_{corr} and J_{cath} values were higher for the 1 mm L-LT sample pre-immersed in sterilised seawater for 1 month than for the 1 mm L-LT sample pre-immersed in Genoa seawater for the same duration time. Furthermore, the passivity plateau was less extended (lower ΔE value) for the sample pre-immersed in sterilised seawater compared to the sample pre-immersed in Genoa seawater. This clearly showed that the layer formed in sterilised seawater was less protective than that formed in Genoa seawater. This conclusion was in agreement with various studies and confirmed that the anticorrosion properties resulted from the layer formed during pre-immersion under the action of the microorganisms [7,26,33]. This was also relevant to the previously observed differences in chemical composition and thickness between the layer formed in sterilised seawater and that formed in Genoa seawater.

To go further with the analysis of the anticorrosion properties of the layer formed during pre-immersion in Genoa seawater, samples were polarised in the anodic domain at a fixed current density of 0.1 mA cm^{-2} for 10 minutes after holding them at the OCP; a confocal microscope was then used to analyse pit propagation.

First, attention was paid to the bare samples. Figure 12 gives average values of pit density, pit depth and pit diameter measured for these samples when they were maintained at the OCP for 5 min before polarisation. Results showed that the standard deviation was very high for both pit depth and pit diameter values. Nevertheless, Fig. 12 (a) shows that the pit density is significantly higher for the 7 mm L-LT sample compared to the 1 mm L-LT sample. This result was associated with lower pit depth values (Fig. 12 (b)) for the 7 mm L-LT samples than for the 1 mm L-LT samples, whereas similar pit diameter values (Fig. 12 (c)) were obtained for both samples. For the 7 mm LT-ST samples, a decrease in both pit density and pit diameter was observed compared to the 1 mm L-LT sample, whereas the pit depth value was significantly increased. From all these results, the main conclusion was that the 7 mm LT-ST samples seemed to promote the in-depth propagation of pits compared to the other samples, which could be associated with the grain size and morphology (Fig. 1). Indeed, for the 7 mm LT-ST sample, pit propagation occurred in the L direction, which was perpendicular to the LT-ST plane. This led to deeper pits because the grains were elongated in this specific direction. This suggested an influence of the grain boundaries on the pit propagation, with the dissolution occurring initially at the grain boundaries, with an extension of the corrosion damage inside the grains. In order to check this hypothesis, EBSD observations were performed for a 7 mm L-LT sample after plotting the anodic polarisation curve in the chloride-containing sulphate solution. Fig. 13 (a) shows a SEM observation of a pit formed on the sample ; Fig. 13 (b) shows the EBSD map of the same region, with the black lines corresponding to the high-angle grain boundaries HAGBs

(misorientation higher than 10°), whereas the grey level referred to the quality of diffraction pattern (band contrast). Superimposition of the SEM image of the pit on the EBSD map (Fig. 13 (c)) clearly showed that the pit propagated following the HAGBs (white circles). Such an analysis was repeated for 20 pits: the same observations were done which strengthened the conclusion concerning the influence of the HAGBs on the pit propagation.

For the samples pre-immersed in Genoa seawater, galvanostatic tests were also performed by applying a fixed current density of 0.1 mA cm^{-2} for 10 minutes after holding the samples at the OCP for 5 min. Only a few large and deep pits were observed on almost all the 1 mm L-LT samples pre-immersed in Genoa seawater, whereas numerous pits were observed for the bare samples for a similar test (Table 2, Fig. 14). It should be noted that, with these experimental conditions, within the limits of the experiments performed, no pit was observed for the 1 mm L-LT sample pre-immersed for 2 months for the light side and 15 days for the dark side. Finally, for the 7 mm L-LT and 7 mm LT-ST samples pre-immersed in Genoa seawater, in most cases, no or only a few pits were observed after similar galvanostatic tests. These results clearly confirmed the efficient anticorrosion properties of the layer formed during pre-immersion in Genoa seawater, as previously demonstrated with the polarisation curves (Figs. 9 and 10). Furthermore, galvanostatic tests performed on the 1 mm L-LT sample pre-immersed for 1 month in sterilised seawater showed more numerous pits than for the 1 mm sample pre-immersed in Genoa seawater (Table 2), with a similar size (Fig. 14 (b)). This again showed the role of microorganisms in the mechanisms of layer growth and the subsequent anticorrosion properties of the layer.

Nevertheless, the absence of pits after the galvanostatic tests for many pre-immersed samples in Genoa seawater raised some questions. To explain the results, the potential was recorded as a

function of time during the tests. Figure 15 shows the results obtained for the 1 mm L-LT sample pre-immersed for 1 month in Genoa seawater. Results obtained for the 1 mm L-LT bare sample and for the 1 mm L-LT sample pre-immersed in sterilised seawater are also given for comparison. Similar conclusions were obtained for the other pre-immersed samples, but the results are not shown for brevity. For the sample pre-immersed in Genoa seawater, the potential increased sharply to a potential of about $4.2 V_{SCE}$, and then stabilised at about $4.5 V_{SCE}$ during the galvanostatic test, showing that the layer formed in Genoa seawater was quite insulating after 5 min of immersion at OCP in the chloride-containing sulphate solution, and retained these properties during the galvanostatic test. This could explain the absence of pits observed after some galvanostatic tests, considering that, depending on the samples, the electrical properties of the layer could vary in accordance with the heterogeneity mentioned earlier. In addition, the results showed that the layer formed in sterilised seawater did not have the same electrical properties, which was relevant with the differences in chemical composition, thickness and electrochemical response described previously. The sample pre-immersed in sterilised seawater rapidly showed similar behaviour to the bare sample, although, during the first 2 minutes of the galvanostatic test, an insulating behaviour was observed. Indeed, a potential peak was first observed, with a maximum potential value of about $2.4 V_{SCE}$ and $0 V_{SCE}$ for the sample pre-immersed in sterilised seawater and the bare sample, respectively, and then the potential stabilised at a value of about $-0.5 V_{SCE}$ for both samples. Such a variation in potential for the sample pre-immersed in sterilised seawater should be due to hydration of the layer during the first few minutes of the galvanostatic test.

To strengthen the analysis, another set of galvanostatic experiments was performed after holding the samples at the OCP for 24 hours. The results showed that the peak was no longer observed for the sample pre-immersed in sterilised seawater, because the longer holding time at

OCP allowed hydration of the layer prior to the galvanostatic test. The hydration of the layer formed on the sample pre-immersed in Genoa seawater was also evidenced for a holding step at OCP of 24 hours, with a lower potential value at the end of the galvanostatic test than in the first galvanostatic test (holding step at OCP of 5 min); however, the potential at the beginning of the galvanostatic test, of about $2.5 V_{SCE}$, was higher than that for the layer formed in sterilised seawater, confirming the differences in properties between the two layers. Furthermore, the analysis of the pits after these galvanostatic tests showed again more numerous pits on the bare sample and sample pre-immersed in sterilised seawater than on the samples pre-immersed in Genoa seawater (Table 2), confirming the better anticorrosion properties of the layer formed under biotic conditions (Genoa seawater). The increase in pit density for the sample pre-immersed in Genoa seawater when the holding time at OCP was increased from 5 min to 24 hours prior to galvanostatic test was related to changes in the electrical properties of the layer due to hydration in chloride-containing sulphate solution.

4. Conclusion

The layer formed in the presence of microorganisms for different times of pre-immersion in natural seawater of a 5083 Al alloy was characterised using SEM-EDS and GDOES, and the influence of the layer growth on the corrosion behaviour of the alloy was investigated. Samples were taken from two different plates, a 1-mm plate and a 7-mm plate: L-LT plane was studied for both plates, and the LT-ST plane was also studied for the 7-mm plate. These samples differed by their microstructures, i.e. grain size and fraction of surface area covered by coarse intermetallics. The results obtained with samples pre-immersed in natural seawater were compared to those obtained after pre-immersion in sterilised seawater in order to assess the influence of the microorganisms. The main conclusions are described as followed:

1. A layer formed during pre-immersion in natural seawater (in Genoa) on the surface of AA 5083 Al-Mg alloy. The layer had a similar structure and composition for 1 mm L-LT, 7 mm L-LT and 7 mm LT-ST samples: it corresponded to an oxy-hydroxide layer separated from the substrate by an interfacial zone. The layer was mainly composed of O and Al, which were homogeneously distributed inside the layer, and also contained Mg, which was found to be segregated in the external part of the layer. S was also found both in the external part of the layer and in the interfacial zone, and Ca was mainly present in the interfacial zone. The layer was thicker for the 7 mm LT-ST samples compared to both 1 mm L-LT and 7 mm L-LT samples, which showed an influence of the substrate microstructure on the formation and growth of the layer.

2. When the 1 mm L-LT sample was immersed in sterilised seawater, i.e. in the absence of microorganisms, a thinner layer formed on the sample surface. This layer was also an oxy-hydroxide layer, but with a lower amount of S and Ca, and a significantly higher amount of Mg. This result demonstrated the influence of microorganisms on the layer growth. However, the mechanisms of layer growth under biotic conditions were not the focus of the study; they will be analysed in future work.

3. As expected, the influence of the substrate microstructure was also observed when the corrosion behaviour of the different bare samples was studied by plotting polarisation curves in 0.001 M NaCl + 0.1 M Na₂SO₄ solution. The 7 mm samples showed a significantly lower corrosion resistance than the 1 mm L-LT sample. These differences were correlated with the higher fraction of surface area covered by IMCs for the 7 mm samples compared to the 1 mm L-LT sample. Furthermore, pits were found to be deeper for the 7 mm LT-ST sample, which was

explained by the influence of HAGBs on the pit propagation: for this plane, pits propagated in the L direction which was the direction of grain elongation.

4. Polarisation curves plotted in the same electrolyte for samples pre-immersed in Genoa seawater, i.e. samples pre-immersed in natural seawater and thus covered by the layer formed during pre-immersion, showed that this layer improved the corrosion resistance of AA 5083 for all the studied microstructures. The corrosion mechanisms were not modified, but it was found that the layer formed during pre-immersion improved the pitting corrosion resistance of all samples pre-immersed in Genoa seawater compared to bare samples. In comparison, samples pre-immersed in sterilised seawater showed significantly lower corrosion resistance, confirming the influence of microorganisms on the formation of the layer with good anticorrosion properties. The analysis of the role of the microorganisms on the layer growth will be the subject of future work.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Credit authorship contribution statement

C. Nkoua: Investigation, Formal analysis, Validation, Visualization, Methodology, Data curation, Writing - original draft, Writing - review & editing. **C. Josse:** Investigation for GDOES

experiments, Formal analysis for GDOES experiments, Validation for GDOES experiments. **A. Proietti**: Investigation for EBSD experiments, Formal analysis for EBSD experiments, Validation for EBSD experiments. **R. Basséguy**: Funding acquisition, Methodology, Formal analysis, Project administration, Supervision, Validation, Conceptualization, Data curation, Writing - original draft, Writing -review & editing. **C. Blanc**: Funding acquisition, Methodology, Formal analysis, Project administration, Supervision, Validation, Conceptualization, Data curation, Writing - original draft, Writing -review & editing.

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