

Corrosion phenomena on aluminium alloys spontaneously mitigated in natural seawater

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Although aluminium alloys are known to exhibit generally good corrosion resistance in natural seawater, they may encounter generalised and localised corrosion phenomena. In this work, an aluminium alloy casted referring to the AA 5083 composition was tested in artificial vs. natural seawater exposed to the photoperiod. SS 254 SMO samples were exposed to the same environments acting as indirect indicator of the bacterial growth by OCP (Open Circuit Potential) ennoblement. OCP and SEM (Scanning Electron Microscopy) data obtained from aluminium alloy revealed that the corrosion phenomena encountered in the NaCl reference solution, mainly consisting of mud crack scaling and rare crystallographic pits, were attenuated in natural seawater. The inhibiting effect probably depended on the organic molecules adsorbing from the bulk and produced by settling bacteria as well.

PAROLE CHIAVE: ALUMINIUM, STAINLESS STEEL, SEAWATER, CORROSION, PROTECTION.

INTRODUCTION

The good corrosion resistance of aluminium alloys is related to the formation of an airborne oxide layer affording a certain degree of protection. The Al-Mg (5xxx) series have been used for many years in marine applications; indeed, they are generally regarded as seawater-resistant alloys [1][2]. In natural seawater, the threat of localised corrosion in presence of chlorides [3] makes this solution a challenging environment for the integrity of aluminium alloys in any case. Referring to corrosion control by inhibitors, environmentally non-impacting products are a research issue [4]. In this view, organic inhibitors have been studied for 20 years [5]. Regarding aluminium alloys, inhibiting organic molecules are demonstrated to be effective, even when they are produced by settling bacteria. Natural seawater is characterised by the presence of both organic molecules enriching the bulk and colonising bacteria. The aim of this research is to evaluate the mitigation of corrosion phenomena on an aluminium alloy in natural seawater due to its biological activity, which was revealed here at the stage of bacterial colonisation by the OCP ennoblement on stainless steel samples.

MATERIALS & METHODS

A ternary alloy Al94.5Mg4.5Mn1 (wt %) was prepared, corresponding to the nominal composition of the commercial alloy AA 5083, and 9 aluminium (AA) samples were obtained. Stainless steel (SS) 254-SMO plates were used to obtain 9 SS

samples which acted as indirect indicators of the bacterial growth by OCP ennoblement. All the samples had measurements of 10x10x1 mm. They were embedded in epoxy resin; their surface was polished down to 1 µm grain size of diamond paste. The electrochemical tests were performed in the

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sea marine station MARECO of the CNR-ICMATE Institute in Bonassola (SP) during October ($T_{\text{seawater}} = 21^\circ\text{C}$). The immersion environments were:

- a 200 L mesocosm filled with natural seawater renewed at a rate of 5 L min⁻¹ exposed to the photoperiod, allowing

the development of shallow seawater photo-biology,

- a 50 L tank filled with NaCl 3.5% wt. solution that was placed inside a 200 L mesocosm acting as a thermostatic bath. The NaCl environment represented the abiotic reference condition (Fig.1).



Fig. 1 - Immersion environments: a) natural sea water, overview of the 200 L mesocosms exposed to the photoperiod; b) natural sea water, internal view of one of the 200 L mesocosms; c) artificial sea water, view of the 50 L tank containing the samples immersed in NaCl solution. This tank was partially immersed in a 200 L mesocosm which acted as thermostatic bath.

The OCP potential was monitored for 8 days on 9 AA and 9 SS electrodes for each environment at a rate of 1 point/h with respect to Ag/AgCl (Ref. through the text). SEM observations

were performed on 3 AA electrodes randomly chosen in each of the two aforementioned environments of exposition.

RESULTS

OCP data, reported as 95% confidential intervals of the mean, μ 95%CI are reported in Figs. 2 and 3 for SS and AA samples, respectively.

Considering the SS samples, those immersed in natural seawater tend to raise their potential from the 4th day of immersion (Fig.2b). This behaviour was not observed on samples immersed in NaCl solution (Fig.2a).

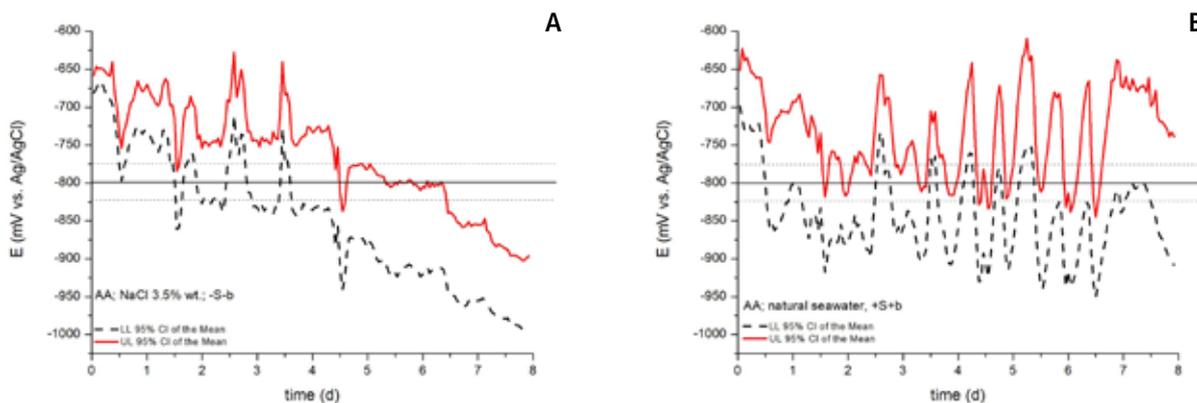


Fig. 2 - 95% confidential intervals of the mean, μ 95%CI, from n=9 sized sample of SS electrodes immersed in: a) artificial sea water; b) natural seawater

Corrosion

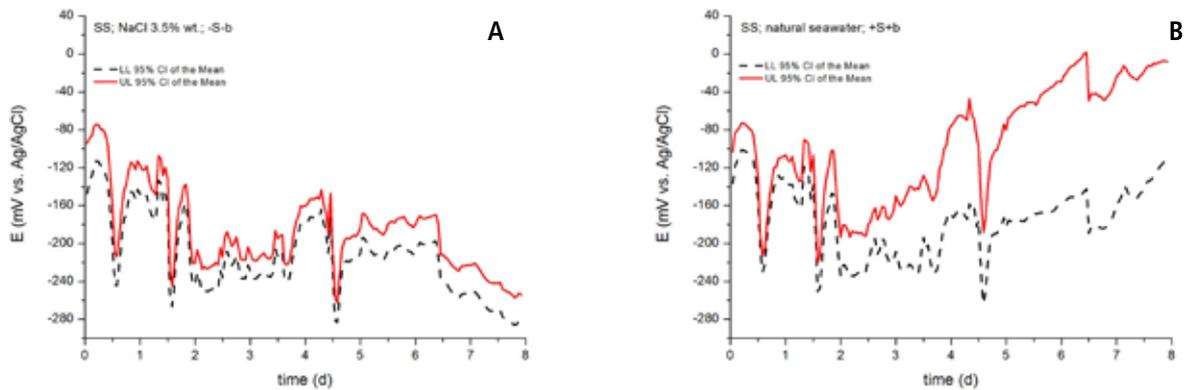


Fig. 3 - 95% confidential intervals of the mean, μ 95%CI, from n=9 sized sample of AA electrodes immersed in: a) artificial sea water; b) natural seawater

AA samples showed a progressive decline of OCP towards electronegative values in NaCl solution (Fig.3a). In turn, OCP trends obtained in natural seawater showed a diminution lasting a couple of days (Fig.3b), thereafter, no more time dependent oscillations were evident.

Considering the morphology of corrosion, all the AA electrodes observed with SEM after immersion in NaCl solution showed wide areas of 'mud cracks' and rare isolated crystallographic pits (Fig. 4).

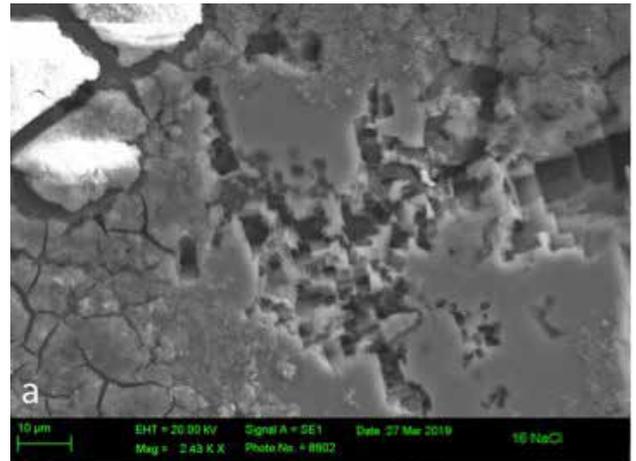
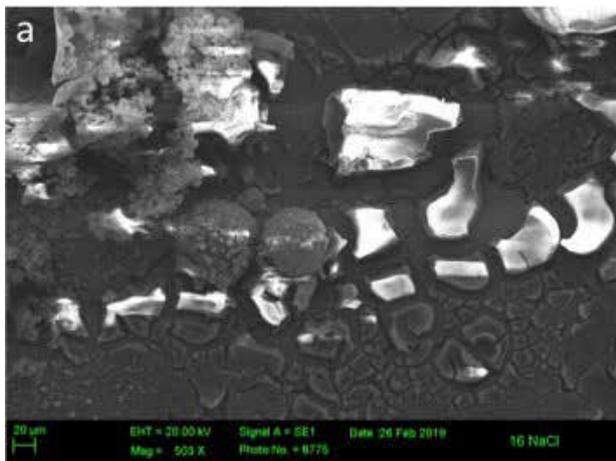


Fig. 4 - Corrosion phenomena observed on AA specimens immersed for 8 days in artificial sea water: a) mud crack areas; b) crystallographic pits.

The samples immersed in natural seawater showed less extended areas of mud crack structures and fewer crystallographic pits

when compared to the samples in the NaCl abiotic environment (Fig. 4).

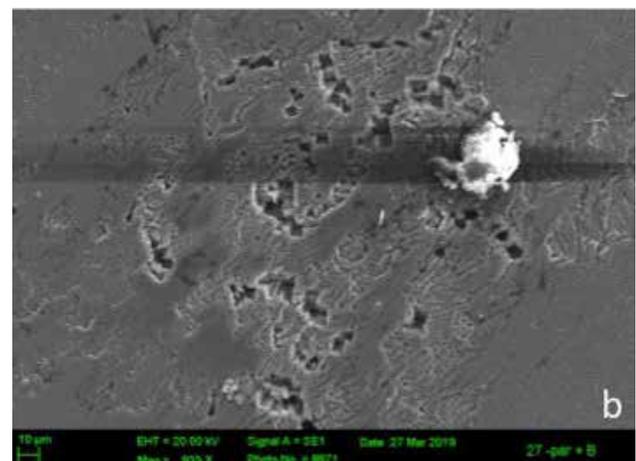


Fig. 4 - Corrosion phenomena observed on AA specimens immersed for 8 days in natural seawater: a) mud crack areas; b) crystallographic pits.

DISCUSSION

The less aggressive corrosion phenomena of AA samples in natural seawater vs. NaCl solution is discussed in view of the coherence between OCP and SEM data.

Pitting formation is possible at potentials lower than pitting potential, E_{pit} , and nobler than repassivation potential, E_r [6], which can be deduced from the data of Treuba et al. [7] [8]: $E_r \approx -800 \pm 56$ mV vs Ag/AgCl.

Hence, about the AA samples immersed in artificial sea water, the pits observed probably formed at potentials higher than E_r , i.e. $E > -800$ mV vs Ag/AgCl, which were met during the first three days of immersion. Successively, OCP continued its downward trend reaching E values lower than -800 mV vs Ag/AgCl, in relation to the expansion of mud crack active areas working as endogenous anode, prohibiting successive pit formation.

Considering the AA samples immersed in natural seawater, pits are thought to have developed for time $t < \approx 3$ days, when OCP was nobler than ≈ -800 mV Ag/AgCl. For higher

times, $t > \approx 3$ days, OCP regularly oscillated around $E \approx -800$ mV Ag/AgCl, probably in relation to the photo-biological activity. As a matter of fact, OCP variations on AA 5083 were observed in seawater exposed to the natural photoperiod in [9]; in the cited reference potentiodynamic sweeps showed a backward shift of the passive branch during the night. Hence, the OCP oscillatory behaviour can be seen as a response of the electrode to the adsorption of molecules, whose inhibiting properties are more effective during particular photo-biological stages, i.e. during OCP maxima. Indeed, organic molecules are studied as corrosion inhibitors in general [10] and also on aluminium alloys [11].

Hence, the inhibiting activity may be due to two organic systems: one coming from organisms enriching the bulk of natural sea water (bulk molecules) [12], and the second produced by organisms like bacteria colonising the electrode surface (biofouling molecules) working directly on aluminium alloys [13], as suggested by [14]. About the second, the OCP ennoblement of SS samples immersed in natural seawater (Fig.2b) revealed the onset of interfacial bacterial activity [15] [16] exhibiting temporal consistence with the onset of OCP oscillations on AA.

CONCLUSION

Ad hoc cast AlMg4.5Mn aluminium alloy, corresponding to the 5083 Al alloy composition, was investigated in seawater along with 254 SMO stainless steel. OCP data and SEM observations showed that the aluminium alloy in natural seawater underwent less aggressive corrosion phenomena than in artificial seawater. It is suggested that the mitigation of

corrosion phenomena in natural seawater probably depended on the biological activity of the seawater, counteracting the corrosive potential related to its halogenic nature. It is supposed that this protection is provided by organic inhibiting molecules coming from the bulk, and, from the bacterial colonisation in relation to their biological/metabolic processes.

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