Reduction of potential ennoblement of stainless steel in natural seawater by an ecofriendly biopolymer

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Abstract :

The effect of biofilm formation on passive stainless steel in seawater environments is of primary importance since it leads to potential ennoblement of surfaces and subsequently to localized corrosion such as pitting and crevice corrosion. This study aims at developing an ecofriendly alginate biopolymer containing both non-toxic calcium and a limited amount of biocidal zinc ions which inhibits this effect. For this purpose, calcium alginate containing less than 1 % of zinc ions localized in the vicinity of the steel surface in natural and renewed seawater is demonstrated to reduce significantly the ennoblement process of steel. After 1 month of immersion, a mass loss of only 4 % of the active material is observed authorizing thereby long-term protection of steel in real environment.

Keywords : Biopolymer, Steel, Ennoblement, Antimicrobial, Alginate, Biofilm

1. Introduction

In a natural environment, microorganisms can grow, develop and then form biofilms on any available natural and man-made surfaces. The presence of such biofilm on passive alloys such as stainless steels in natural seawater strongly enhances the cathodic reaction of oxygen [1]. This leads to an increase of the open circuit potential (so called ennoblement) by about 350 mV [2-7] and consequently to the initiation of pitting corrosion showed by Xiangbo *et al.* [8], the ennoblement process is highly dependent on the growth of bacteria on the metal surface and thus follows an exponential law. This phenomenon was used for decades to monitor the biofilm growth in seawater at its initial phase, and thus trigger some water treatments [9-14]. However, the mechanisms responsible for the ennoblement process are quite complex. Among them, the oxygen reduction reactions in the biofilm seems to play a major role [15,17]. The influence of enzymes and more recently electron transfer on the process was also clearly demonstrated [18,19].

Traditional chemical treatments of biofilm are based on the use of biocides. They are particularly efficient when applied at the initial phase of the biofilm formation. Indeed, bacteria in biofilm can be a thousand times more resistant than their planktonic counterparts [20]. However, such treatments lead to a biocide dosage escalation and consequently to environmental issues and propagation of resistance [21]. Thus there is an urgent need for the development of new eco-friendly materials with antifouling properties [22] and to explore novel strategy to combat this phenomenon [23, 24]. Biopolymer integrating silver nanoparticles can be produced for that purpose [25,26]. However, the eco-friendly nature of such material is still debatable [27]. Recently, we proposed a solution based on a biopolymer, *e.g.* alginate, containing several types of cations [28]. The anti-adhesive and biocidal properties of this material was assessed in laboratory towards microalgae strains, and promising results were obtained against *Cylindrotheca closterium* which acts as pioneer microalga strain in surface colonization [29, 30]. This previous study showed that a mixed zinc/calcium alginate protects the surfaces by blocking the microalgae adhesion together with a low toxicity, an essential property for environmental friendly applications. The present study aims at demonstrating the ability of proposed alginate-based solution to reduce the ennoblement process of stainless steel in a natural and renewed seawater i.e. in conditions representative of real applications. For this purpose, the measurement of the corrosion potential of stainless steel was performed with and without alginate active materials in the vicinity of the samples. Moreover, to highlight the

influence of non-toxic calcium ions in the reduction of the ennoblement process, alginates containing only zinc or zinc and calcium ions are considered.

2. Materials and methods

Alginate is a copolymer composed of α-L-glucuronic acid (G) and β-D-mannuronic acid (M) linked together in different sequences via 1–4bonds. The formation of zinc alginate and calcium/zinc alginate from a sodium alginate solution is based on the adsorption of positive ionic species on anionic groups of the alginate polymer. The reaction is governed by the ion exchange process between sodium cations and the other cationic species, in this case: Zn^{2+} and Ca^{2+}. This leads to the jellification of the biopolymer. Briefly, a solution of sodium alginate (Sigma Aldrich 71238, M/G ratio of 0.85) was prepared with a concentration of 0.25 mol.L^{-1} by magnetic stirring during 5 hours. Solutions of $CaCl_2$ and $ZnC_4H_6O_4$ were added to the sodium alginate solution in order to modify the initial sodium alginate. A concentration of 0.1 mol.L^{-1} of $Zn(C_4H_6O_4)$ was used for zinc alginate (ZnAlg) while concentrations of 0.27 and 0.05 mol.L^{-1} of $CaCl_2$ and $Zn(C_4H_6O_4)$ were used for calcium/zinc alginate (CaZnAlg). The elaborated hydrogels were rinsed with deionized water to remove the excess of ions on the surface.

UNS S32205 duplex stainless-steel (DSS) coupons were polished and subsequently immersed in 3 liters seawater tanks. The natural seawater was continuously renewed at 1.5 L/h using peristatic pumps. A tank containing two UNS S32205 coupons without any alginate was used as reference. In two other tanks, four cubes of alginate (1 cm^3) were positioned near the coupons (at 3 cm), without a direct contact. The open circuit potential or corrosion potential (Ecorr) was monitored during 30 days using a voltmeter with a high input impedance ($> 10^8$ Ω) EPC8 from nke Instrumentation. Saturated Calomel Electrode (SCE) reference electrode from Mettler Toledo were used as reference. Following these measurements, the morphology and the chemical composition of the biofilms were determined using Scanning Electron Microscope (SEM) imaging. The crystalline structure of the material was analysed by X-ray diffraction (XRD) with an Empyrean PANalytical apparatus using the CuKα radiation. The chemical characterization of the polymer was obtained by X-ray photoelectron spectroscopy (XPS). Briefly, the experimental apparatus consisted of an Al-Kα ray source (Thermo VG) and a cylindrical mirror analyzer from RIBER.

3. Results and discussion

The surface morphology and chemical composition of the dried hydrogels was studied before their immersion by SEM/EDX. As shown on Fig. 1 of supplementary information, the surface of the material is very smooth. The hydrogel's composition is presented in Table 1 : the materials are mainly composed of carbon and oxygen atoms due to the hydroxyl and carboxyl groups of the alginate matrix. The presence of zinc and calcium cations is clearly observed and explained by the ion exchange process between Na^+ present in the initial alginate and the cations present in the solution. Atomic percent of 1.6 % of Zn^{2+} was found for the ZnAlg. Values of 4.1% and 0.8% of Ca^{2+} and Zn^{2+} were measured for CaZnAlg. Note that the decrease of zinc content in CaZnAlg with respect to ZnAlg is in agreement with the zinc concentration in the two solutions used to produce the materials. XPS measurements, not shown here, proved the presence of Ca^{2+} and Zn^{2+} species in agreement with the exchange process. During sorption of ionic species by hydrogels, as observed for silver ions, nanoparticles may form [26]. In this case, XRD patterns reveal the presence of nanoparticles. In the present work, XRD patterns were measured but do not present any structure indicating the absence of such nanoparticles.

	C	O	Zn	Ca	Cl
ZnAlg	65.8	32.6	1.6		
CaZnAlg	58.0	34.0	0.8	4.1	3.1

Table 1. EDX results achieved on ZnAlg and CaZnAlg.

Fig. 1(a) displays the variations of the E_{corr} potential of steel coupons with the immersion time. Without any alginate hydrogels in the surrounding environment, as shown by the pink curve, a potential ennoblement with values above 0.3 V/SCE is obtained after 12 days of immersion time. This behavior is frequently observed during the biofilm formation on stainless steel in natural seawater [31] and corresponds to the well-known ennoblement process. As stated by Xiangbo et al. [8], an exponential law correlated to the development of bacteria on the surface describes the potential variation. The blue line in Fig. 1(a) displays the potential variation when zinc enriched alginate cubes are placed in the vicinity of the steel coupons. In this case, the potential ennoblement is clearly delayed in time, demonstrating thereby the ability of ZnAlg alginate to inhibit the biofilm growth during the initial stage of its formation. This confirms the biocidal action of the material observed in laboratory conditions [28] on adhesion of microalga on glass and on their growth in Guillard's F/2 medium at 2% [32]. The use of

zinc/calcium (CaZnAlg) alginate leads to a different behavior. Firstly, an additional delay is observed in the ennoblement process. Secondly, the increase of the E_{corr} potential remains very low with respect to the two previous cases. This reduction of the ennoblement is of first relevance when considering the possibility of pitting corrosion since it remains even after 30 days of immersion time showing the long-term efficiency of the CaZnAlg alginate.

The reduction of the ennoblement process is associated with the release of the calcium and zinc cations in the surrounding environment, as it is also made for the development of controlled release systems for drugs in medical applications. The biocidal action of the modified alginate is attributed to the release of Zn^{2+}, calcium ions being ineffective regarding this effect. In contrast, both calcium and zinc cations inhibit the adhesion of microalgae on surfaces as demonstrated in laboratory tests [28]. Due to this mode of action, the efficiency of the materials should be highly dependent on their solubility. To investigate such property, the mass of the alginate cubes was measured before and after the 30 days of immersion. Mass losses of 4% and 38% were determined for CaZnAlg and ZnAlg, respectively. As the consequence, the higher efficiency and long term activity of CaZnAlg with respect to ZnAlg seems therefore associated to the low solubility of the material in seawater despite a lower content of biocidal agent.
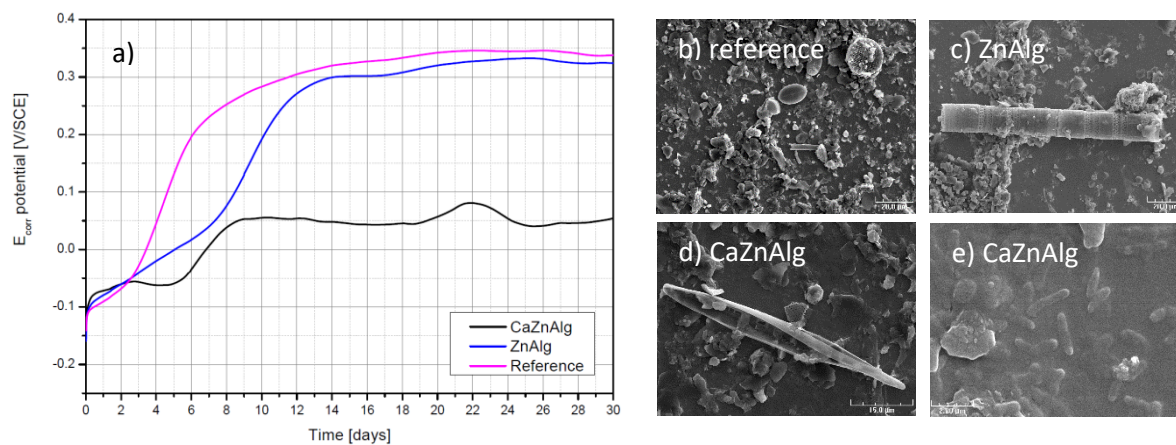
Fig. 1. a) E_{corr} potential variation *versus* immersion time in natural seawater for a steel coupon without any additional material (reference), with zinc alginate (ZnAlg) and calcium/zinc alginate (CaZnAlg) in vicinity of the coupons. b,c,d) SEM images of these three steel coupons showing the presence of diatoms. e) marine bacteria visible on the film treated by CaZnAlg.

To investigate the surface of the steel coupons after the ennoblement process, SEM images of surfaces after biofilm formation were analysed (see Fig. 2 of supplementary data).

Large area images show that the surfaces are fully covered by a biofilm. This leads to an increase of the roughness with respect to the initial surface. Several regions of the surfaces were probed at the micrometer scale. Fig. 1(b,c,d) displays some representative images of the surfaces for the three cases discussed above. As observed, the surfaces are covered by a complex matrix composed of biomacromolecules and microorganisms. Pennate diatoms dominate and this is in agreement with Landoulsy *et al.* [33 and references therein]. Pennate diatoms have the ability to attach to the substrate *via* extracellular polymeric substances which are secreted by their raphe slits. In particular, *Actinocyclus exiguous* and *Rhizosoleniineae* were identified in the present work. The influence of CaZnAlg on the biodiversity within the biofilm is depicted in Fig 1(e). Indeed, as observed, the SEM image does not display only diatoms but also the presence of bacteria in the surface. Such bacteria were absent from the two other surfaces (untreated and treated by zinc alginate). The lower value of E_{corr} achieved with the presence of CaZnAlg in the surrounding environment might therefore be associated with a different composition of the biofilm with more bacteria and less diatoms. However, a full quantification of microorganism would be necessary to confirm this finding. Note that, the influence of diatoms on the ennoblement process with respect to that of bacteria was reported in the pioneering investigation of Ishihara and Tsujikawa [34, 35]. Indeed, these authors demonstrated the strong increase of the E_{corr} potential when considering diatoms plus bacteria within the biofilm instead of only bacteria. However, as pointed out by Landoulsy *et al.* [33,36], separating the influence of both species on the ennoblement process is not straightforward.

4. Conclusion

As a conclusion, the reduction of the ennoblement process on stainless steel is clearly highlighted when positioning CaZnAlg material near the steel surface in natural and renewed seawater. A mass loss of only 4% is reported after one month indicating the long-term activity of the biomaterial. This result greatly exceeds our expectations following our laboratory tests, carried out in a well-controlled and closed environment, and opens up prospects for new developments of this environmentally friendly hydrogel for in situ applications in real conditions. As demonstrated, a higher content of biocide agent in the alginate does not provide a better efficiency. In contrast, the influence of the anti-adhesive property of CaZnAlg alginate associated with its low solubility seems to be the most important criterion for the development of such materials. However, characterization of the biofilm property and it's composition will

be our next goal for research as these data will be key to further understand and characterize the interaction between the biofilm and the active material.

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