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Microbiologically Influenced Corrosion in Aluminium Alloys 7075 and 2024

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Abstract

Aluminum and its alloys are central materials for the aircraft industry. Aluminum alloys (AA) 7075 and 2024 are widely used both in the structures and in brittle sections of the airplanes. The presence of the alloying elements in these metals makes them susceptible to localized corrosion at the same time vulnerable to bacterial attachment. A great number of reports on aircraft deterioration are related to microbial growth by contamination inside fuel storage tanks and aircraft wing tanks; this phenomenon is known as microbiologically influenced corrosion (MIC). As expected, corrosion and biocorrosion increase maintenance costs and time of the aircraft in the hangar. Therefore, the growing interest is to shed light on these issues and develop future inhibition methods. In this chapter, we will give an overview of microbiologically influenced corrosion associated with AA 2024 and 7075 by consortia and bacteria. Three mechanisms of biocorrosion in aluminium alloys have been described. In addition, some alternatives methods to battle the effect of biocorrosion will be shown, these methods are based on green compound which blocking of attached of bacteria and promote the detachment of biofilm, being these a tendency of the last innovation way to inhibit this kind of phenomenon.

Keywords: microbiologically influenced corrosion, aluminum alloy, mechanism, 2024, 7075, inhibition of biocorrosion

1. Introduction

Aluminum and its alloys have a good corrosion resistance owing to aluminum oxide passive films. Unfortunately, the susceptibility of these materials to localized corrosion makes them particularly vulnerable to microbiologically influence corrosion (MIC). The phenomenon of MIC involves the acceleration and/or alteration of corrosion processes resulting from the



presence and activities of microorganisms with the generating a biofilm at the metal surface [1]. This phenomenon has been documented for metals exposed to different media, for instance, groundwater [2] and industrial waters [3]. The MIC is not a new kind of corrosion, although the deterioration of metal substrate is caused by an increase in the kinetic of the corrosion process by the presence and the metabolic activity of the microorganisms. These effects can be critical and therefore are important to consider the conditions and roles of microorganisms in the corrosion [4]. The consequences of microbiologically influenced corrosion are pitting corrosion, crevice corrosion, and de-alloying corrosion and correspond to localized corrosion type.

The kinetic of corrosion is determined by the characteristic of the physical chemistry environment at the interface. This environment can be clout by the parameters of concentration of oxygen, salts, pH, redox potential, and conductivity. All these factors are, at the same time, influenced by growing microorganisms [4]. The organisms can attach to surfaces, embed themselves in slime and so-called extracellular polymeric substances (EPSs) [5]. The EPS, usually called "biofilms," plays an important function of cell adhesion [6], biofilm formation [7], and protection of microorganism from adverse environment [8]. Biofilm formation consists of a sequence of steps and begins with adsorption of macromolecules (proteins, polysaccharides, and humic acids) and smaller molecules (fatty acids and lipids) at surfaces [9]. Both adsorbed molecules and biofilms can change the physical chemistry characteristics of the interface, including surface hydrophobicity and electrical charge. The amount of adsorbed organic material is a function of ionic strength and can be enhanced on metal surfaces by polarization. The biofilms formed on a metallic surface can be very thin (monolayers) but can reach the thickness of centimeters [4]. Thus, biofilms, characterized by a strong heterogeneity, are very complex system and require analysis in order to characterize and clarify which component could be available to influence some steps of the redox reaction or how could be the change of characteristic of the oxide passive films.

The characteristics of the surface of metallic substratum play an essential role in developing the biofilm during the early stages of EPS accumulation and may influence the rate of cell accumulation and distribution [10]. There is a vast amount of literature investigating the influence of metallic surface properties on the interaction with microorganisms, of which are, chemical composition, roughness, wettability, and polarization.

The microorganism requires metal ions for it is development. The colonization of a metal surface is likely affected by the presence and free availability of metal ion or salts [11]. Gerchakov et al. evaluated the chemical composition of metals substratum which impacted the microfouling formation rate and the cell distribution in samples exposure to seawater environment. This influence was markedly detected during the first hours of exposition [12]. Moreover, the chemistry of the metallic substrate alters the bacteria viability on the metal surface in favor or opposing, because the chemistry can improve the attachment of cell by the interaction of biofilm [13], and on the other hand, preventing the colonization as a result of the toxic element, for instead, chrome [14].

Other parameters that may influence the rating process of bacterial accumulation on metal are the surface free energy, which is as reflected by hydrophobicity or hydrophilicity and surface roughness. Mueller et al. determined the rate coefficient of adsorption, desorption, and growth for early bacterial colonization on different metal surfaces (copper, silicon, 316 stainless steel, and glass) with different roughness. They found that this parameter correlated positively with biological adsorption process [15]. The topography of surface on microbial attachment has been studied by Nickels et al. in silicate grain shape on the distribution of a microbial community. The roughness is related to the pattern and texture of a surface, and it is inherent to both obtaining, by incorporation of alloying elements and aging process of aluminum alloys. The higher surface roughness could increase the quantity of bacterial accumulation due to the better adhesion that took place at surface irregularities; nevertheless, other authors found reduced adhesion to rougher surfaces [16].

It is well known that the metabolic activity of biofilm clusters can change the pH value for more than three units locally. This means that directly at the interface, where the corrosion process is actually taking place, the pH value can differ significantly from that in the water phase [4]. Thus, water sample pH values do not reflect such effects [17].

However, these phenomenon not are the total of observation, for instead, in some cases, the interaction of bacteria with metal surfaces causes increased corrosion rates, but it has been observed too that many bacteria can reduce corrosion rates of different metals and alloys in many corrosive environments [18], but it is dependent on exposure time because the positive or negative effect is closely related to metabolic activity and mature biofilm.

This chapter is intended for readers interested in the impact of microorganisms on the corrosion processes. A review of the main mechanisms associated to microbiologically influenced aluminum alloy corrosion will be given. Therefore, it is expected that this text can be used for those requesting an introduction to the subject of MIC related to aluminum alloys. On the other hand, some attractive mitigation methods of biocorrosion in aluminum alloy will be presented, thinking of a new methodology with a "green" approach.

2. MIC related to aluminum alloy 2024 and 7075

Most reports of MIC found on aluminum alloys (AA) 2024 and 7075 are used in aircraft or in underground fuel storage tanks. The microorganisms are introduced in to fuel tanks from airborne contaminants, and through water, that enters the tank [19]. The accumulated water inside fuel tanks (building with AA 2024-T3) induces the growth of microorganisms and may lead to microbiologically induced corrosion (MIC) of these tank structures. In the past, jet fuel contaminants have been reported to include a diverse group of bacteria and fungi, with the most common contaminant being the fungus *Hormoconis resinae* [20]. However, Rauch et al. [21] investigated microbial contamination in the United States Air Force (USAF) aviation fuel tanks. They found 12 genera, including four *Bacillus* species and two *Staphylococcus* species.

The most interesting part of this work is related to the kind of bacteria found in comparison to another study carried out in 1950 [22]. Changes in the microbial community constitution may demonstrate microbial adaptation to variations in fuel composition, particularly additives and biocides, enabling the material to be dominated by bacteria. Microbial proliferation in aircraft fuel storage tanks leads to deterioration of fuel quality and corrosion of aluminum alloys [23].

In contrast, the corrosion of AA 7075 has been evaluated in the presence of fungi *Cladosporium resinae* [24] and bacteria. Hagenauer et al. [25] in a joint project of different European aircraft manufacturers studied the involvement of microorganisms in aircraft corrosion damage. This study found that a total of 208 microorganisms among them 158 bacteria, 36 yeasts, and 14 fungi are collected from corroded sites of 7 different airplanes. The results show that the corrosive effect of the isolated microorganisms of the genera *Micrococcus, Enterococcus, Staphylococcus, Aerococcus, Bacillus, Aspergillus,* and *Penicillium* induced strong corrosion toward AA 7075.

Material degradation and/or metallic corrosion involve the transfer of electrons that release metal ions into the surrounding medium but, how far microorganisms promote corrosion in airplanes in practice is hard to prove, and more investigations concerning the microflora of corroded sites as well as the underlying corrosion promoting mechanisms have to be conducted. Today's scientific challenge rests in clarifying the interactions and roles of the metallic surface with the microbial activity that affects the kinetics of electron transfer reactions such as cathodic and/or anodic reactions, resulting in material breakdown.

Different mechanisms have been proposed to explain the microbial corrosion process of aircraft aluminum alloys: (i) oxygen concentration cell, (ii) organic acids, and (iii) extracellular enzyme activity.

2.1. Oxygen concentration cells

A mature biofilm restricts the diffusion of oxygen toward cathodic sites. The oxygen concentration cells formed between the zones covered by the microorganisms and the uncovered zones as a consequence of the fungus respiration have been reported by Miller et al. [26]. Iverson et al. [27] reported the presence of tubercles on the bottom of jet fuels tanks containing sulfate reducing-bacteria which corrode materials through the formation of electrochemical oxygen concentration cells, and cathodic depolarization due to the bacterial sulfate reducers. **Figure 1** shows the adsorbed cells and biofilm formation on the metallic surface. The non-uniform bacterial colonization results in local anode and cathode zones with the formation of differential aeration cell. Under aerobic environment, areas under respiring colonies become anodic reaction (metal dissolution), and surrounding areas become cathodic (oxygen reduction reaction) [28].

Therefore, the formation of differential aeration cell is intrinsic to the development of the film and is one of the first mechanisms to be postulated because it does not depend on the metabolic wastes or activity of the microorganisms, since the only presence of the biofilms on the metal surface has the potential to produce this kind of mechanism by itself.

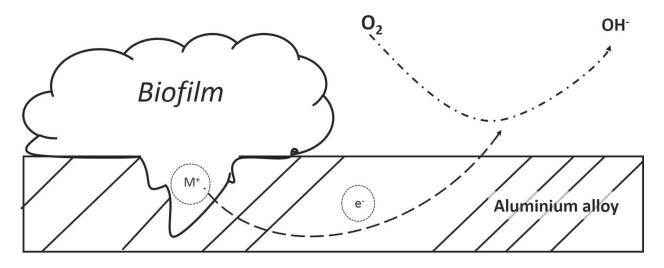


Figure 1. The physical presence of microbial cells on a metal surface as well as their metabolic activities, modify electrochemical processes. The adsorbed cells grow and reproduce, forming colonies that constitute physical anomalies on a metal surface, resulting in the formation of local cathodes or anodes.

2.2. Organic acids

Another mechanism related to microbial corrosion of aluminum alloys is the production of organic acids, which are metabolized by the microorganism. Most heterotrophic bacteria secrete organic acids during fermentation of organic substrates. The kind and amount of acids depend on the type of microorganisms and the available substrate molecules. Organic acids may force a shift in the tendency for corrosion to occur. The impact of acidic metabolites is intensified when they are trapped at the biofilm/metal interface. Furthermore, fungi are ubiquitous in atmospheric and aquatic environments where they assimilate organic material and produce organic acids including oxalic, lactic, formic, acetic, and citric acids. McKenzie et al. [29] found the production of citric, cis-aconitic, isocitric, and α -Ketoglutaric acid with *C. resinae* growing in the jet fuel. These acids are able to facilitate an alloy pitting corrosion through a decrease in the pitting potential of aluminum alloys [30].

The organic anions produced by metabolic activity are able to activate the passive aluminum. Schiapparelli and Meybaum [31] proposed a chemical reaction between the metal surface and organic acid, which could be controlling the corrosion process, this reaction is expressed in the next Eq. (1);

$$n X^{-} + Al \rightarrow Al X_{n}^{-(n-3)} \xrightarrow{H_{2}O} Al (OH)_{3} + 3 H^{+} + n X^{-}$$
 (1)

Where *X* is the aggressive anion of a metabolic product from bacteria. The compound formed by the reaction between the anion and the aluminum would be of the non-stoichiometric type and produced pitting and is independent of the electrolyte used. Eq. (2) shows the kinetics of the pit growth that approaches the Engell-Stolica relation [32].

$$i = At^b$$
 (2)

From Eq. (2), "i" is the current density measured at the whole electrode, and "A" and "b" are constants. Therefore, the presence of anions does not change the kinetics of pit growth, showing an exponential coefficient approximately equal to 1. It is generally accepted that the rate of pit propagation follows Eq. (2) and, the exponential coefficient b is a constant dependent on pit geometry.

Citrate and oxalate anions are able to form soluble complexes with the aluminum ions. The experimental results using citrate, oxalate, and acetate anions show that these anions act as pitting inhibitors increasing the pitting potential of 2024 alloys in neutral chloride solutions toward more positive values [30]. Similar results were reported by Rudd and Scully for aluminum in chloride solutions containing citrate anions. The inhibitory effect of acetate and oxalate anions in neutral media can be explained by the formation of a precipitation type compound [33]. On the contrary, acetic and oxalic acid increase the corrosion rate of aluminum which depends on the pH value. In the acid solutions, pitting occurs at more negative values than in neutral chloride solutions. The acidity can prevent the re-passivation process facilitating pitting. Besides, in the acid solutions, pitting can be accomplished by the formation of soluble complexes between the organic acid anions and the aluminum cations, thus increasing the dissolution rate [34]. Moreover, another investigation also reported an increase of the pitting potential of aluminum in presence of chloride solutions as the acetate concentration increases [35].

2.3. Enzymatic activity

Two mechanisms for microbiologically influenced corrosion of aluminum alloys has been largely documented, which are (a) production of water-soluble organic acids and (b) formation of differential aeration cells. Nonetheless, a recent study has inquired a mechanism related to enzymatic activity as metabolic product of bacteria.

Enzymatic activity is evidenced in the formation of corrosion products and has been considered one of the most important processes and a key to explain the microbial corrosion of aluminum alloys. Hedrick et al. [36] found that the transformation or dissolution of certain metallic atoms can be linked to the presence of extracellular enzyme by comparing the degree of attack to the magnesium content of different in aluminum alloys, given the importance of magnesium ions in microorganism growth.

In a recent work carried out by our group, we isolated and identified an aggressive bacteria to AA 7075-T6. The bacteria were found in corrosion product of a drain valve from military aircraft, and it is closely related to *Bacillus megaterium* species [37]. *B megaterium* bacteria have been declared before, by other authors, as fuel tank microbial contaminant of the United States Air Force aviation [21]. The presence of this type of bacteria in fuel tanks and drain valves [23] could be caused by changes in refinery practices and chemical composition of fuels or possibly by the increased use of fuel additives [20]. In the laboratory study using *B. megaterium* and AA 7075-T6, the results showed, after 14 days, an increase of the corrosion current nearly to three orders of magnitude in comparison with sterile control. By electrochemical

impedance spectroscopy (EIS), we found that this microorganism can change the pH in the interface. The enzymatic activity could be related to this change.

Bacteria have evolved specific mechanisms to prevent production and adverse effects of reactive oxygen species (ROS). Catalase is an integral component of the bacterial cell response to oxidative stress, and together with superoxide dismutase and alkyl hydroperoxidases, it is thought to limit the accumulation of reactive oxygen species, such as hydrogen peroxide (H_2O_2) by catalyzing its decomposition to water and oxygen [38]. An adapted schematic representation of the proposed catalase mechanism by Busalmen et al. is shown in **Figure 2** [39]. It is commonly accepted that oxygen reduction can proceed through a parallel mechanism involving the direct reduction via four electrons and a pathway where intermediate peroxide is formed. In this last case, oxygen electro-reduction proceeds by the transference of two electrons producing H_2O_2 as an intermediate compound and then to hydroxyl ions by the transference of two more electrons and ultimately increasing the local pH to alkaline conditions [40].

A schematic representation of the proposed catalase mechanism in a metallic surface is shown in **Figure 2**. It is commonly accepted that oxygen reduction can proceed through a parallel

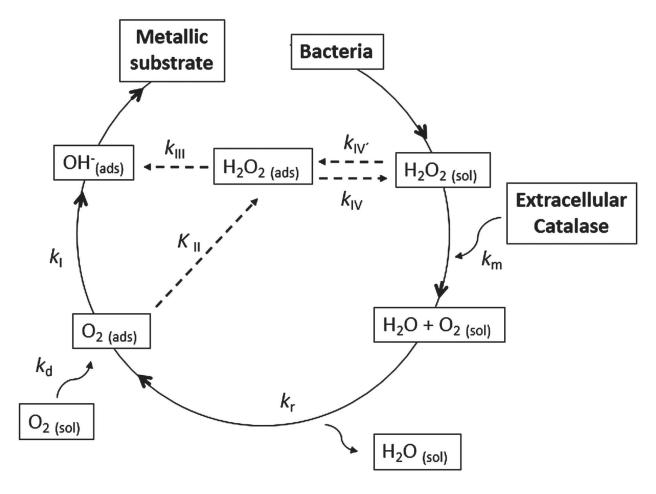


Figure 2. Proposal of microbial corrosion mechanism for catalase. The electrochemical reduction of oxygen to OH⁻ is coupled with the enzymatic decomposition of hydrogen peroxide by an autocatalytic cycle. Kn is the rate constant at their respective step (n). Species in solution (sol) or adsorbed to the metallic surface (ads) are indicated.

mechanism involving the direct reduction via four electrons and a pathway where intermediate peroxide is formed. In this last case, oxygen electro-reduction proceeds by the transference of two electrons, with the production of H_2O_2 as an intermediate compound (k_{II}) , and then to hydroxyl ions by the transference of two more electrons. In the figure, the rate constant k_{III} represents the second two electrons transferred, yielding low levels of H_2O_2 in solution. The electro-reduction of peroxide can be inhibited depending on the composition of the surface oxides, favoring its desorption to the solution (k_{IV}) . The catalase mechanism is based on the enzymatic conversion of electrochemically produced H_2O_2 to water and oxygen in the proximity of the surface (Km).

3. Future in mitigation methods

Among the strategies to mitigate or control the effects of MIC in material using aircraft industry, biocides are the most widely applied. This approach aims to reduce microorganisms in both, number and type within a given system. In general, biocides may be inorganic compounds such as ozone, chlorine, and bromine, and organic compounds such as isothiazolone, quaternary ammonium, and aldehydes (glutaraldehyde and acrolein), which have the ability to disrupt cellular physiology by disrupting the membrane of the cell, interfering with cellular metabolic processes, or by interrupting the ability of the cell to generate energy in the form of ATP [41]. One of the problems associated with the use of biocides is the inability to effectively penetrate biofilms. Furthermore, due to the high toxicity of antibacterial applied in the industry and in view of complex environmental, ecological, and economic constraints placed by international organizations, great efforts have been focused on the development of benign biocides to prevent bacterial colonization and subsequently the formation of biofilms [42]. In recent years, a number of biocides that could be used to mitigate biocorrosion in the aeronautical industry have been proposed.

3.1. Enzymatic activity inhibition

One of the most interesting strategies of biocides is their action as enzymatic activity inhibitors. Although these compounds do not eliminate the bacteria, they do however reduce their metabolic activities rendering them harmless. A compound with potential development and application in the aeronautical industry is capsaicin compound. The capsaicin (**Figure 3**) is known as the main component of red pepper species (Capsicum species). It is composed of three major functional moieties, namely, a vanilloid, an amide, and a hydrophobic side chain. Capsaicin and its synthetic derivatives have been extensively investigated in the fields of pharmacy [43], neuroscience [44], and antimicrobial drugs [45]. At present, following the evaluation of inhibition of zebra mussel attachment, capsaicin showed the most promising activity, being highly antifouling (EC50 13.7 mM) but weakly toxic toward mussels and water fleas [46] and consequently may be more promising as an environmentally friendly antifoulant [47].

Studies carried out using microalgae *P. tricornutum* showed that the reactive oxygen species (ROS) levels were significantly increased in nonivamide (Capsaicin)-treated algae [48]. Algal

$$H_3C(H_2C)_7$$
 H
 OCH_3

Figure 3. Capsaicin structure.

antioxidants, including catalases (CAT), peroxidases (POD), superoxide dismutase (SOD), and glutathione (GSH), were all stimulated by the ROS burst. The overproduction of ROS substances can consume large amounts of metabolic energy and also lead to the loss of photosynthetic pigments and lipid membrane damages, thereby inhibiting algal growth.

3.2. Colonization and biofilms formation inhibition

The composition of the biofilms is due to the combination of the following: active secretion, shedding of cell surface material, cell lysis, and/or adsorption of substances from the environment like organic and inorganic compounds. EPSs usually include organic acid with functional groups, such as carboxylic and amino acids that readily bind metal ions. EPSs are also related to increased biofilm resistance to biocides and other antimicrobial compounds [49]. Therefore, the adherence of bacteria on the metallic surface could be the key to blocking many metabolic activities of the bacteria that ultimately lead to aluminum alloy corrosion. There are currently two methods by which it possible to inhibit the action of bacteria to colonize the surface, (a) the modification of the metallic surface toward a super-hydrophobic surface or (b) use p-amino acids to prevent the biofilms formation. The first case, the super-hydrophobic modified metallic surface could prevent the attachment of microorganism on the aluminum alloy. The second case, the use of p-amino acids could lead a breakdown of a biofilm formed on a metallic substrate, and/or the presence of specific quantities could avoid the development of biofilm.

3.3. Super-hydrophobic surface

The sorption of microorganisms to surfaces is an important factor in microbial adhesion on the metallic surface. This task is accomplished by an initial reversible phase of bacterial sorption to the solid surfaces which are time-dependent, following a cell growth, and finally an irreversible phase of sorption of some of the bacteria [50]. After that, the development and growth of biofilms take place.

The considerable importance of characteristic of the surfaces in corrosion resistance, the super-hydrophobic modified surface, inspired by nature, is one the most interesting strategies to avoid corrosion [51]. Superhydrophobic surfaces, with water contact angles (CA) greater than 150°, are recently interest due to their self-cleaning character. In order to generate such a modified surface, including micro- and/or nanostructures, or low surface energy coating should be considered. Many attentions are now focused on the design of microstructure surface with the advancement of nanotechniques, such as chemical vapor deposition, chemical etching, template-based extrusion, and electro-deposition [40].

Surface wetting behavior can generally be broken down into different regimes, based on the value of water contact angle (WCA). Two traditional regimes are the hydrophilic and hydrophobic regimes, defined as WCAs in the range of $10^{\circ} < \theta < 90^{\circ}$ and $90^{\circ} < \theta < 150^{\circ}$, respectively. Hydrophobic coatings are intensively used in plenty of engineering applications; moreover, they are widely used in paint and varnish industries. Although hydrophobic and hydrophilic regimes comprise a vast amount applications, superhydrophobic and superhydropholic regimes, which describe the extremes surface wetting behavior, are much more interesting. Superhydrophilicity, which is characterized by WCAs in the range of $\theta < 10^{\circ}$, within 1 s of the initial wetting, describes nearly perfect wetting. In contrast, superhydrophobicity, described by WCAs of $\theta > 150^{\circ}$, describes a state of nearly perfect nonwetting (**Figure 4**) [52].

Corrosion resistance can be improved by introducing the anticorrosive coatings on the surface of aluminum and its alloys, e.g., preparing the chromate-based coatings or surface anodizing [53]. Chromate-based coatings can provide highly effective corrosion protection, but environmental regulations are increasingly restricting their use, while the anodization will increase the weight of the aluminum and its alloys. Given the strong water repulsive property of the superhydrophobic surfaces, they make a promising technology for slowing the breakdown of the native aluminum oxide layer and thereby retarding corrosion of the aluminum layer underneath. As a result, the anticorrosion performance of aluminum and its alloys may be improved due to superhydrophobic surfaces which inhibit the contact of a surface with water, environmental humidity, and corrosive medium. However, in these cases, either special equipment/complex process control is required, or caustic or costly reagents, for instance, HNO₂, HF, H₂O₂, or fluoride are needed. Consequently, these methods/procedures may result problematic as either pollution or expensive methods. Therefore, a simple, inexpensive, and environment friendly fabrication method is quite needed, since it is very advantageous for industrial large scale production. Herein, work with a novel method for the preparation of super-hydrophobic surfaces on the aluminum alloys is very important.

Some work has been reported on the fabrication of super-hydrophobic aluminum surfaces using chemical etching techniques. The aforesaid chemical etching technique is an inexpensive and simple method to produce artificial super-hydrophobic coatings. Recently,

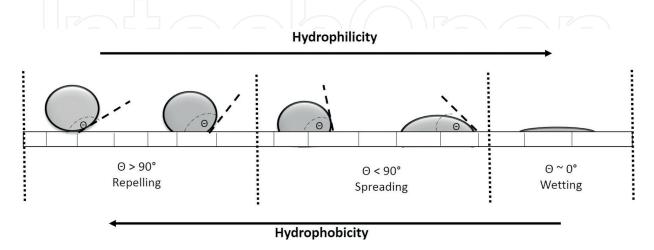


Figure 4. Schematic of contact angle (CA) for a water drop placed on surfaces of different hydrophobicity.

Xie et al. [54] developed super-hydrophobic aluminum surface by a chemical etching process using NaOH solution as an etchant and lauric acid as a low surface energy material. Wang et al. [55] worked on aluminum alloy using stearic acid. Their results showed long time stability and excellent resistance to corrosive liquids including acidic, basic, and salt solutions. The procedures are fairly facile to carry out, and no special technique or equipment is required. Moreover, only the ordinary reagents, such as the boiling water, ethanol, stearic acid, etc., are used in the procedure (**Figure 5**). The methods are also environmental friendly, while the as-fabricated super-hydrophobic aluminum alloy surface could confer excellent corrosion resistance. Therefore, the methods using super-hydrophobic modified surface are a promising alternative due to involving the main step of attachment of bacteria on a metallic surfaces of aluminum alloys.

3.4. p-Amino acids

In all life kingdoms, organisms predominantly use and synthesize L-type enantiomers of amino acids. On the other hand, D-type amino acids are accumulated in millimolar quantities in the supernatant of bacterial cultures in stationary phase, and whose function is to modulate the synthesis of peptidoglycan (PG). PG is a strong and elastic polymer and main component structural supports of bacterial cell wall, controlling the turgor and stability of cell wall in front to change of the environment.

About of the application of D-aminoacids, as both, corrosion and biocorrosion, not much evidence that show to these amino acids as corrosion promoters [10]; on the contrary, authors suggest that p-amino acids have inhibitors effect [17]. Zhuo et al. studied peptides of 12 amino acids in length which are bind to aluminum inhibiting the corrosion [56].

Lam et al. found that bacteria *Vibrio cholerae* produce p-methionine and p-leucine, while *Bacillus subtilis* produce p-tyrosine and p-phenylalanine [57]. These amino acids produced by bacteria are a common strategy to adapt in changing environmental conditions. Moreover, a mix of p-amino acids can control the biofilms formation or breakdown. Kolodkin-Gal et al. found that *Bacillus subtilis*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* produce a mix of p-amino acids between leucine, methionine, tyrosine, and tryptophan, which prevented the biofilms formation and could break down existing biofilms [58]. Cava et al. evaluated how extracytoplasmic processes regulate the biofilm formation; the authors also showed that p-amino acids are secreted outside of bacteria and perform to regulate the biofilms [59]. **Figure 6** shows a representative mechanism of the p-amino acids proposed by Cava et al.

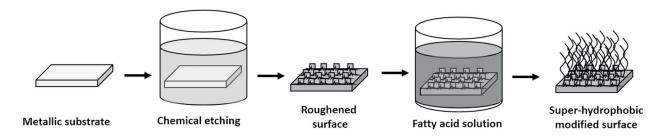


Figure 5. Schematic diagram of simple method to obtain super-hydrophobic modified surface.

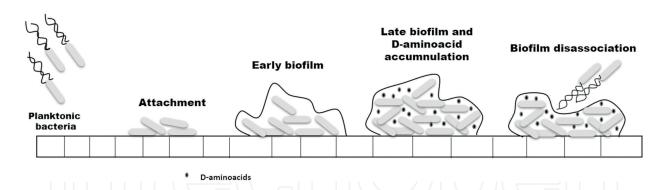


Figure 6. Schematic representation of the mechanism of p-amino acids in the breakdown of biofilms.

The detachment of the biofilm from the substrate has been studied. Xu and Liu evaluated the p-tyrosine in the detachment behavior of biofilms of *Vibrio harveyi* [60]. These studies showed that p-tyrosine has two effects, inhibited microbial attachment and promoted biofilm detachment, and in addition, the production of EPS was significantly suppressed.

Considering the potential of p-amino acids as inhibitors in biocorrosion is due to their low toxicity. Studies have used mixtures of p-amino acids together with corrosion inhibitors. Xu et al. tested a mixture of p-methionine and tetrakis hydroxymethyl phosphonium sulfate (THPS) for biocorrosion inhibition of carbon steel exposure to *Desulfovibrio vulgaris* [61]. The author concludes that the binary mixture of p-amino acid and THPS prevented biofilm formation and removed pre-established biofilms from surfaces, and it also reduced MIC pitting of the carbon steel coupon. Further investigation by Xu et al. showed that applying a mixture of p-amino acids and THPS is more effective in developing biofilm inhibition than using either compound on its own. The amino acid cocktail in question is being constituted by p-tyrosine, p-methionine, p-tryptophan, and p-leucine [62]. These results offer significant candidates in the search for efficient biocides, since one of the problems that arise with the use of these treatments is the deactivation of biocides by the biofilms.

4. Conclusions

Aluminum and its alloys are susceptible to microorganism attached, as both fungus and bacteria. The susceptibilities have been related to the chemical composition of the alloy and the morphology and topography of the surface associated with roughness parameters. Report of attaching of microorganism on aluminum alloy is fuel line system, mainly due to the fuel is a source food but is not enough to microorganism growth and development of biofilms, also some salts are necessary, for instead, magnesium salts. The magnesium could be obtained from the metallic substrate. On the other hands, the role in the bacterial activity of another metal present in the surface of an alloy is not clear. In fact, the knowledge related to antibacterial properties of the intermetallic (θ phases, rich in copper) in AA 2024-T3 is poor, and at the same time, the role of the intermetallic containing zinc metal in AA 7075-T6.

The interactions of the alloys and bacteria, in most of the cases studied, cause a detrimental by the influence of the microorganisms in corrosion phenomenon. The biocorrosion has been widely studied, and the research shows a correlation of microorganism activity and corrosion acceleration. The microbiologically influenced corrosion in aluminum and its alloy are related to three mechanisms: (a) Differential oxygen cell, (b) weakening of the aluminum oxide films by the presence of organic acids, and (c) extracellular enzyme activity which including the catalase enzyme. However, some articles indicate that sulfate reducing bacteria as responsible for corrosion in aluminum and copper containing alloys such as Monel [63]. The anaerobic bacteria activity in biocorrosion of aluminum alloys is not clear, and it is very interesting to evaluate the anaerobic bacteria in consequences of degradation of organic materials as fuel and corrosion of aluminum alloys.

The primary effect of the microorganisms is the destabilization of the aluminum protective oxide film either mechanically or chemically. Once biofilm is formed on the metallic substrate, a local corrosion is developed. The local corrosion of aluminum alloy is a catastrophic problem in the aircraft industry.

The interdisciplinary studies are essential to understand the biocorrosion phenomenon and the main proposed mitigation strategies and methodology including different scientific area as engineering, chemical, and biological. Effective methodologies to inhibit the adverse effect of the microbiologically influenced-corrosion have not been developed. The creation of effective methodologies is a great challenge, due to the biocorrosion phenomenon is a complex with many variables, and moreover, the plan of action should include green methods (reagent and procedures).

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