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CORROSION OF STEELS INDUCED BY MICROORGANISMS

Biljana S. Maluckov*

Technical Faculty in Bor, University of Belgrade, Vojske Jugoslavije 12, 19210 Bor, Serbia

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Abstract

Diverse types of steels have found application in industry owing to their ability to form passive films resistant to the electrochemical corrosion. However, the presence of microorganisms in the production environment can cause undesired corrosion of metals. Therefore, any information on the chemical structure of corrosion products and microbiological deposits, as well as the estimation of the biocorrosion level can be extremely useful in applications. To prevent or reduce biocorrosion the initial selection of the materials and design of the technological equipment are of crucial importance. At later stages it is shown that proper and regular cleaning of the equipment is a necessity. This would significantly lower cost for reparation of the equipment damaged by the microbial action.
Key words: Biocorrosion, Steel, Sulfate reducing bacteria.

Introduction

The bacterial cells can colonize the metal surfaces causing their damage [1]. During the colonization of the solid surfaces the population of microorganisms increases rapidly forming a kind of biofilm which covers the attacked surface [2]. This process is usually defined as biocorrosion, i.e. the microbiologically induced corrosion (MIC) [3].

If the microorganisms are in the aqueous solution, they first attach to the surface and then grow, replicate and produce exopolymers (EPS), forming a cohesive structure known as a bioflm [4]. This process depends on the surface characteristics of substrates, including metal surface free energy, roughness, hydrophobicity, and metallurgical features [5]. In other words, the biocorrosion is the result of the synergetic interactions of the metal surface, abiotic corrosion products, bacterial cells and cells metabolites [3]. In general, the metal surfaces are mostly affected by bacteria existing in land and water as the sulfate-reducing bacteria (SRB), iron oxidizing/reducing bacteria,

* Corresponding author: Biljana S. Maluckov, bmaluckov@tf.bor.ac.rs

manganese-oxidizing bacteria, and bacteria that secrete mucus and organic acids [6]. Moreover, the investigations have been shown that mentioned bacteria species coexist in biofilms forming complex structures on the corrosive metal surfaces [3]. In addition**,** **t**he literature results show that the combination of SRB and iron-oxidizing bacteria produces a higher level of corrosion than the SRB or iron oxidizing bacteria acting separately [7, 8].

The deterioration of steel structures in fresh water and marine environments is crucially dependent on the biocorrosion processes. In industrial practice, due to their importance and effects these processes attract special attention [9]. Studies have shown the complexity of the microbiologically induced corrosion in different environments. Related to this, each particular case of biocorrosion requires development of the unique approach [10]. Here is a brief review of the techniques developed for investigation of the biocorrosion processes on steel components in different environments.

Typically applied microscopic techniques provide a qualitative assessment, while the surface chemical technique provides qualitative and quantitative estimations of the characteristics of the biofilm formation, transport and electrochemical corrosion processes [11]. Biofilms formed in different environments under either field or laboratory conditions on naturally occurring and man-made surfaces have been extensively studied in various stages of their development using a wide range of microscopy techniques [12]. However, the conventional microscopy techniques do not allow visualization of the bacteria cell surfaces or events involved in the MIC in the real time, such as pitting initiation, or synthesis of the extracellular polymeric substances [13]. On the other hand, the microscopic techniques based on the optical epifluorescence microscopy (OEM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provide elemental (SEM, TEM) and two-dimensional (TEM) data about surfaces and objects. However, these techniques either do not have sufficient resolution (optical microscopy) or require sample preparation (SEM and TEM) so they cannot be used on-site [1]. Lack of SEM is a long sample preparation and sample distortion caused by the dehydration process. Optical microscopy does not have problem with collecting the sample, but cannot give the power magnification as the SEM techniques do [9, 13]. Atomic force microscopy (AFM), environmental scanning electron microscopy (ESEM) and confocal laser scanning microscopy (CLSM) can be used for observation of biofilms in real time without changing the sample structure [14]. The ESEM technique ensures high resolution images for detailed observation of biofilms in the full hydrating form (without the dehydration process) [9, 13]. CLSM and AFM allow the examination of hydrated biofilms and provide clean, three-dimensional images of living biofilms in real time [6]. Microscopically obtained data on the type of microorganisms, combined with the data from the chemical analysis of surfaces [6], and electrochemical measurements [6, 15, 16] provide information about the chemical composition of the corrosion products and microbiological deposits, and can be used to estimate the level of corrosion. The electrochemical reactions involved in the corrosive processess caused by microorganisms can be clarified by obtaining information on the chemical structure of corrosive products and microbiological layers, as well as by quantifying the coorosion rate.

Corrosion of steel caused by microorganisms

The wide application of various types of steel in industries is a consequence of their ability to create passive thin films resistant to electrochemical corrosion. The austenitic stainless steels are defined as iron alloys containing at least 16.5% chromium and up to 13.5% nickel. In addition, molybdenum may be added to increase the resistance to pitting and crevice corrosion of steel [1]. These stainless steels (SS) are largely used in sugar and agricultural industry. At each step of the production process line reed juice tends to favor corrosion in many parts of equipment. In sterile juice the pitting corrosion of SS304L samples does not appear, while in the old and the fresh juice it is detected indicating the corrosion activity of microorganisms. Aging juice reduces its pH and the steel sample becomes less resistant to corrosion. Fig. 1 shows the texture and arrangement of species growing on the surface of the SS304L [17]. From the technological point of view, the reduction of the contact time between the juice and surface can prevent the effects of the juice aging [17]. Analysis of the localized corrosion mechanism of stainless steel types SS304L and SS316L in the presence of iron-oxidizing bacteria *Sphaerotilus spp*. isolated from rust deposits in clogged carbon steel heat exchanger from an oil refinery plant (Haifa, Israel) showed that SS316L is characterized by stronger passivity and, therefore, with more improved resistance to pitting attack by the iron bacteria in comparison with SS304L [18]. Xu et al. [7] showed that the combination of sulphate-reducing bacteria (SRB) *Desulfovibrio sp.* and iron oxidizing bacteria (IOB) of the *Leptothrix sp.,* which were isolated from the system for cooling water in the refinery, induce a higher degree of corrosion of SS316L than each of mentioned bacteria species separately. By adding 0.01 M NaCl, as the result of synergy between constituents 0.01 M NaCl + SRB + IOB, the highest level of corrosion has been obtained. This indicated that the chloride anions accelerate the pitting effect [7]. In sea waters, the corrosion potential of stainless steel can be increased to several hundreds millivolts. The corrosion potential changes only to a small extent in the filter- or heat-sterile pasteurized seawater which is used for experimental control [15]. Although, there are several possible explanations for increasing of the corrosion potential of stainless steel in natural sea water, all authors agreed that the main cause are changes in the cathodic reaction on the metal surface due to the microbial activity [19]. The investigations of the MIC on the steel SS304L with marine aerobic *Pseudomonas* bacteria NCIMB2021 have shown that the thickness of the passive films on steel samples is lowered by mutual attack of these bacteria and anions in sea water. Therefore**,** it is proposed that the *Pseudomonas* bacteria are involved in the oxidation/reduction reactions of iron [20].

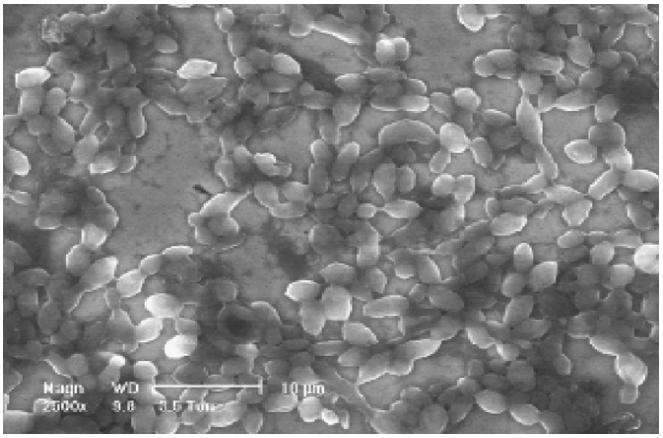

Fig. 1. High surface density population growth of a colony on the surface of SS304L observed under ESEM [17].

Duplex stainless steel (DSS) is often used in cases where the contact with chloride leads to cracking of austenitic stainless steel pitting corrosion and/or stress corrosion. This is a good alternative to the austenitic stainless steels in aggressive environments [21]. The ESCA (Electron Spectroscopy for Chemical Analysis) studies of 2205 DSS samples, which were continuously exposed to the chloride medium containing SRB species *Desulfovibrio desulfuricans* for 40 days, indicate that metal sulfides, mainly iron sulfides, are incorporated in the passive film. Sulphidization passive film depolarizes the cathode reduction reactions induced by H_2 or H^+ [21]. Fig. 2. shows the SEM images of the specimens exposed for 40 days to SRB and images obtained in the sterile conditions. After removing the biofilm etching of duplex structure and micropits were observed. Also local areas of black coloured surface film were noticed. Etching of duplex structure was more clearly visible under the film. The low Cr and Mo phase (austenite) was appeared as islands in the etched duplex structure, observed under the black coloured surface film, as indicated by '1'. Whereas the similar regions indicated as '2' have high Cr and Mo level (ferrite) [21].

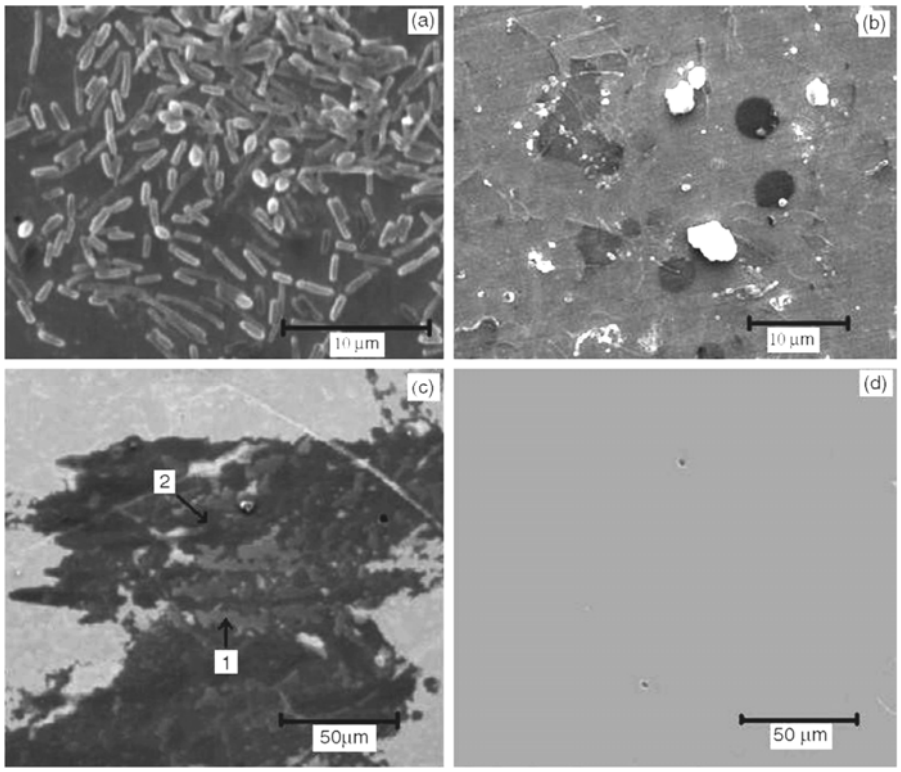

*Fig. 2. SEM image of (a) cell bodies attached on the coupons after 3 days of exposure; (b) biofilm observed after 40 days of exposure in medium containing SRB**;** (c) surface condition after removing the biofilm and (d) coupon exposed to sterile medium for 40 days [21].*

Mild steels are steels with the low carbon content. The mild steels and carbon steels are also broadly used in industry. The main triggers of corrosion of these steels are sulfate reducing bacteria (Fig 3.). The SRB types show considerable adaptability to extreme conditions. Among them the SRB, *Desulfovibrio sp.* can be relatively easily isolated and purified [22].
SRB is metabolized in the following way:

$$4H_2 + SO_4^{2-} + 2H^+ \rightarrow 4H_2O + H_2S, \quad (1)$$

(The role of hydrogenase)

or:

$$2Laktat + SO_4^{2-} + H^+ \rightarrow 2Acetate + 2CO_2 + 2\,H_2O + HS^-, \quad (2)$$

where lactate is an electron donor [23].

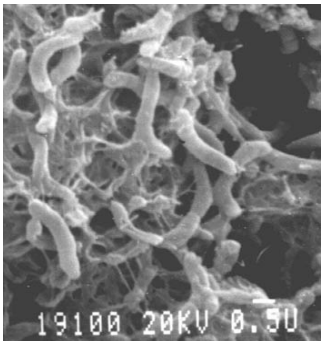

Fig. 3. Biofilm formed by sulfate-reducing bacteria on the surface of mild steel, visualized using SEM [6].

The activity of enzymes involved in the metabolism of S and H is one of the main factors which determine the activity of the living cells *Desulfovibrio*. It was found that the level of H_2S production is directly proportional to the specific activity of the enzyme, and that the degree of microbiologically induced corrosion of carbon steel is directly proportional to the bacterial resistance to the metal ions [24]. The structure of the medium affects the corrosion of steel by sulphate-reducing bacteria. Results obtained in sterile and inoculated media without sulfate were similar. On the other hand, in the presence of sulfate it is indicated that the reductions of SO^{2-}_4 and $S^{2-}$and/or H_2S are key processes in the SRB induced corrosion [25]. The presence of thiosulfate increased biocorrosion, which was probably the main factor in the SRB corrosion process [14]. Under nutritionally rich and oligotrophic growing conditions of *D.alaskensis* a risk of localized corrosion of SAE1010 steel charcoal process is latent. However, oligotrophic conditions can cause more serious and harmful localized corrosion processes [26]. Ilhan-Sungur et al. [27] found that the concentration of Zn of 27.8 ± 0.046 mg/ cm^2 in the biofilm was toxic to the pure species *Desulfovibrio sp.* On the other hand, it has been found that mixed SRB species can survive in the biofilm with very high concentration of Zn (162.96 ± 1.88 min.-max**.** 1166.77 ± 2.48 mg/cm^2). It seems that the effect of Zn on the SRB varies depending on the types of SRB and their growth conditions. Therefore**,** this appears as a main reason for corrosion of galvanized steel, although originally it was thought that the galvanized steel is resistant to biocorrosion [28]. Circuit cooling systems of nuclear reactor at Kalpakkama had a problem which included a pipeline blockage due to the formation of tubercule, damping of valve and separator, formation of the holes in the pipe and a high degree of corrosion of the carbon steel piping. Problems arose due to the presence of iron oxidation, sulfate reducing bacteria (*Desulfovibrio sp.)* and exopolymer produced by *Pseudomonas aeruginosa*. The SEM examination filamentation showed the growth of bacteria impregnated with the iron corrosion products (Fig. 4). With increasing thickness and growth inside tubercule environment becomes anaerobic and favored the growth of SRB. Typical SRB-induced pitting in the form of large radial pattern of increasing carbon steel [8] was detected. Under some circumstances, the corrosion of iron and steel can serve as a resource for all macronutrients necessary for bacterial growth, including fixed carbon, fixed nitrogen and phosphorus. Experimental data illustrate that levels of phosphorus released from corroding wrought iron are significant relative to that necessary to sustain high levels of biofilm bacteria. Consequently, it may not be

possible to control regrowth of bacterials on iron surfaces by limiting phosphorus in the bulk water [29].

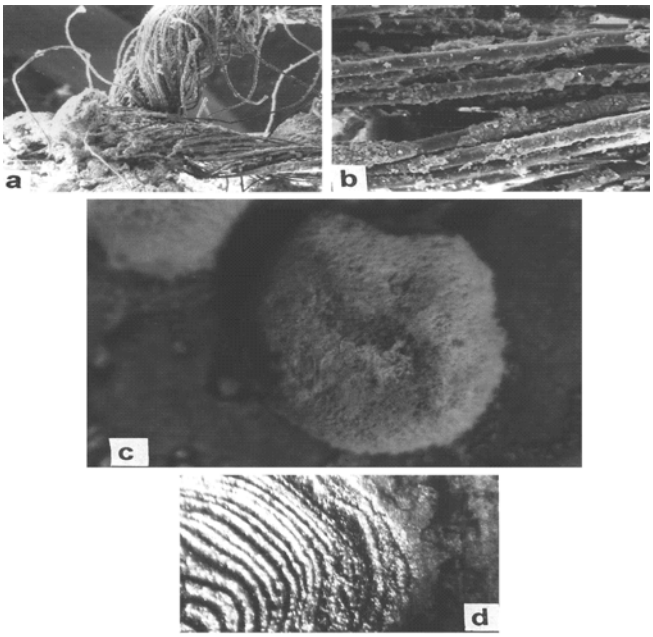

Fig. 4. (a) SEM micrograph showing the holdfast structure by which the iron bacteria filaments attach to the metal surface and colonise, (magnification 1225X, 15 kV); (b) SEM micrograph showing the iron bacteria filaments running parallel on the carbon steel surface. The filaments are encrusted with corrosion products which are mainly iron oxides and hydroxides, (magnification 1750X, 15 kV); (c) micrograph showing iron bacteria tubercle on the carbon steel coupon; (d) Stereo zoom micrograph of carbon steel coupon showing typical SRB induced shallow concentric rings (magnification 40X) [8].

Prevention and control of biocorrosion

The population growth of the microorganisms is inevitable in the living conditions [30]. Therefore the biocorrosion of metal surfaces becomes significant problem in industrial environments. It can irreversibly damage metal surfaces highly increasing the cost of production processes. Bearing in mind this fact, the prevention of the bacterial growth on surfaces should be in the focus of research interest. One possibility is the selection of materials which are insensitive to the biocorrosion. Also**,** the proper technical design of the production setup can help to avoid situations that favor microbial growth and contamination in the system as the stationary conditions, cracks, or lack of adequate drainage. The regular cleaning in association with previously mentioned preventive measures can additionally optimize production process [31]. Physical and chemical methods can be used for fixing antimicrobials on solid surfaces [32].

Generally, the methods commonly used to prevent and control microbial corrosion can be divided into several categories: (i) cleaning procedures, (ii) biocides [33], (iii) coating, and (iv) cathodic protection [31].
However, microorganisms themselves can lead to corrosion inhibition. Microorganisms can contribute to corrosion inhibition by neutralizing the action of corrosive substances present in the environment, forming protective films or stabilizing a pre-existing protective film on a metal, and inducing a decrease in the medium corrosiveness. Finally, the proper understanding of the identity and role of microbial contaminants present on the metal surface can be exploited to induce corrosion inhibition by bacteria to prevent MIC effects [34].

Conclusions

The ability of steel to form a passive layer in the oxidative conditions is highly exploited in industrial applications. However**,** in the living environment the growth of microorganisms on the surfaces is inevitable. They form biofilms that corrode the surfaces. Microscopically obtained data on the type of microorganisms, combined with the data from the chemical analysis of surfaces, and electrochemical measurements provide information about the chemical composition of the corrosion products and microbiological deposits, can be used to estimate the level of corrosion. In order to prevent or reduce biocorrosion selection of materials and design of technological equipment, as well as the proper and regular cleaning of the equipment are of the extreme significance.

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