Corrosion Science 80 (2014) 60–70

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Electrochemical and fractographic analysis of Microbiologically Assisted Stress Corrosion Cracking of carbon steel

Marko Stipaničev [a,c], Omar Rosas [b,c,*], Regine Basseguy [c], Florin Turcu [a]

[a] Det Norske Veritas, Johan Berentsens vei 109-111, 5163 Laksevåg, Bergen, Norway
[b] National Center for Education and Research in Corrosion and Materials Performance, The University of Akron, 264 Wolfledges, Akron, OH 44325, USA
[c] Laboratoire de Génie Chimique CNRS – Université de Toulouse (INP, UPS), 4 Allée Emile Monso, BP 84234, 31234 Toulouse Cedex 4, France

ARTICLE INFO

Article history:
Received 6 May 2013
Accepted 13 November 2013
Available online 21 November 2013

Keywords:
Carbon steel
Microbiological corrosion
Pitting corrosion
Stress corrosion

ABSTRACT

This study was carried out to evaluate the effect of microorganisms on the corrosion behavior of carbon steel when exposed to mechanical axial stress. Open Circuit Potential (OCP) and Electrochemical Frequency Modulation (EFM) response were measured on the tensile specimens while applying a constant load in various environments inoculated with different sulfidogenic or iron reducing microorganisms. The fractographic analysis revealed a noticeable impact of the enriched environments on the topography of tensile specimens; however, after the tests were carried out, it was not possible to detect any indications of a Stress Corrosion Cracking (SCC) failure mechanism for the tensile specimens.

1. Introduction

The damage caused by corrosion to marine steel infrastructure, such as offshore oil production installations, is indisputable. Approximately 20% of the total corrosion cost in this industry is due to Microbially Influenced Corrosion (MIC) [1,2]. MIC is generally found and identified as the localized attack that is associated with the presence of surface-associated biofilms, e.g. microbial communities embedded in a bioinorganic matrix [3].

During oil production, besides the presence of bacteria, mechanical stresses are often seen as an additional component affecting the integrity of the material that leads to failures due to Stress Corrosion Cracking (SCC). SCC is a type of corrosion failure mechanism caused by a complex combination of factors including metallurgical, mechanical and environmental factors. The complexity of SCC has led over the years to numerous hypotheses, models, theories, and controversy on the mechanisms by which SCC occurs. Among them, the dissolution of anodic sites on the metallic surface was sometimes claimed to be the origin for SCC [4]. When carbon steel is exposed to stresses and simultaneously to aggressive environment, the localized electrochemical dissolution of iron can result in mechanically initiated oxide film breakdown that leads to exposure of fresh anodic material to the corrosive medium [5]; in biotic conditions the localized electrochemical dissolution of metals (pitting) may be caused by the tubercle conditions that often lead to pitting corrosion; pitting is the predominant morphology of MIC [6]. The colonization of the metallic surfaces by bacteria and thus development of a biofilm may change the chemical conditions at the interface metal/environment. Biofilm can create gradients of concentration of species across its thickness (100–400 μm) and the pH under the biofilm can decrease inducing severe corrosion conditions underneath the localized biomass.

A few more merging aspects regarding SCC and MIC acting on metal surfaces exist. Besides of their importance for SCC mechanism, microstructure irregularities, such as MnS inclusions, serve as initiation points for pitting in abiotic corrosion [7,8] and during MIC [9]. Avci et al. [9] suggested that, in presence of sulfidogenic bacteria, the initiation of an anodic reaction (dissolution of the metallic iron (Fe) matrix) and the subsequent pitting of steel in the surrounding areas of MnS inclusions is due to the disorder and strain exerted on the Fe matrix by MnS regarded as a contamination of the interface from metallurgical processes. Therefore, it is possible to assume that mechanical stress and bacterial activity may target the same locations on the material surface and synergistically accelerate the deterioration process. Moreover, hydrogen is playing a different but important role in MIC and SCC deterioration processes jeopardizing both, the material integrity and the mechanical properties [10]. This is often associated with absorption of hydrogen in metal structures, which is known as hydrogen embrittlement [11]. The SCC and MIC environments support corrosion reactions due to capability to produce hydrogen in

* Corresponding author at: National Center for Education and Research in Corrosion and Materials Performance, The University of Akron, 264 Wolfledges, Akron, OH 44325, USA. Tel.: +1 3308613175.

E-mail addresses: uberpomar@hotmail.com, orosascamacho@uakron.edu, omar.-rosas@uakron.edu (O. Rosas).

0010-938X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2013.11.009

various circumstances [10], for example, ferrous material being subject to tensile stress in an environment supporting the proliferation of hydrogen consuming Sulfate-Reducing Bacteria (SRB). Tensile stresses coupled with biological activity are an example of the synergic effect between SCC and MIC that may be responsible for producing a local distribution of hydrogen [10].

Despite the wide variety of bacteria found in aqueous environments, Sulfate-Reducing Bacteria (SRB) seem to have received extensive attention from the corrosion community due to their abundance in industrial facilities and in the oil and gas industry; however, the efforts for studying this type of environments have focus on either, the microbiological side or the electrochemical side; a combined study of electrochemical, topographical and mechanical characteristics of materials has not being carried out, especially considering recently developed electrochemical methods. Javaherdashti et al. [4,12] used pure and mixed cultures of SRB in Slow Strain Rate Testing (SSRT) on carbon steel, stainless steel and duplex steel finding that such materials are likely to fail in a shorter time compared to abiotic systems. However, these studies could be improved by estimating corrosion rates through electrochemical characterizations of systems under stress. On the microbiology side, focusing on one type of bacteria seems to limit the effect of bacteria other than SRB, such as iron reducing bacteria (IRB).

IRBs, such as *Geobacter sulfurreducens* ATCC 51573, have been widely studied for their use in microbial fuel-cells due to its electron exchange capabilities with solid substrates [13]. On the other hand, their role in corrosion process is still uncertain. Electrochemical tests have shown that these bacteria can exert two different effects: (i) accelerating the cathodic reaction on the material hence, increasing the corrosion risk; and (ii) shifting the pitting potential towards positive values, which may be interpreted as a reduction of localized corrosion risk. In the absence of an electron donor these bacteria promote the propagation of pitting whereas in the absence of electron acceptor is able to delay pit occurrence [14]. Since bacteria can assist pitting and therefore lead to SCC it is imperative to understand the role of bacterial activity on the Microbiologically Assisted Stress Corrosion Cracking (MASCC). For these reasons, studying the effect of different microorganisms on the corrosion of materials exposed to mechanical stress is imperative and the tool to complement this study is the use of electrochemical techniques.

Open Circuit Potential (OCP) has been used in corrosion studies for long time, especially for detecting potential ennoblement [15] which, is the tendency of the electrode potential to become more positive. Ennoblement of ferrous metals in presence of biofilms most often leads to reaching the breakdown potential leading to crevice or pitting corrosion initiation. On the other hand, Electrochemical Frequency Modulation (EFM) [16,17] is a rather new technique used for corrosion monitoring in various environments and conditions [18,19]; however, there are just few references for EFM used for monitoring MIC [20] and none for carbon steel specimens exposed to biotic environments while being under tensile stress. An advantage of using EFM resides in the small polarizing signals and its ability to provide promptly corrosion currents and causality factors (considered to be a factor determining measurement reliability), all in a single experiment. In addition, preliminary knowledge of kinetic parameters, e.g. Tafel slopes, are not required. Since EFM possess a non-aggressive nature (minor system perturbation), it could be a promising method to monitor corrosion rates in environments supporting biological activity and therefore development of MIC. The current study comprises a combination of mechanical, topographical and electrochemical descriptions for S235JR carbon steel, when subjected to a constant load, in presence and absence of bacteria. Pure cultures of SRB, *Desulfovibrio alaskensis* AL1 and *Desulfovibrio desulfuricans* ATCC 27774, as well as IRB pure culture of *G. sulfurreducens* and consortiums selected from water injection systems of the North Sea Oil and Gas (O&G) industry were used. A constant-load ring was used to apply a uniaxial stress on a tensile specimen while measurements of OCP and EFM were simultaneously carried out.

2. Materials and methods

2.1. Test material

Carbon steel S235JR rod (original diameter 2 cm) (Descoure and Cabaud, France) was used to fabricate rounded tensile specimens with the dimensions shown in Fig. 1. The composition and reported mechanical strength of the material are shown in Table 1. Specimens were ground manually using SiC paper of increasingly fine grain, ending with 600-grit and then rinsed with sterile deionized water to eliminate remaining debris from the grinding process. The specimens were exposed for 24 h to UV light (wave length 256 nm: XX-15, sterilization UV lamp, UVP, USA) at 25 °C before being introduced in the test vessels for sterilization.

2.2. Microbial cultures and growth media

Desulfovibrio desulfuricans ATCC 27774 and *D. alaskensis* AL1 were provided by Bioin Departamento de Química Faculdade de Ciências e Tecnologia Universidade Nova de Lisboa. *G. sulfurreducens* ATCC 51573 was purchased from DSMZ (Deutsche Sammlung von Mikroorganismen und Zellkulturen). Consortiums used in experiments originated from pigging debris collected in water injection pipeline.

Saline modified-VMNI medium (2% or 3.5% NaCl) [21] served as a growth media for the pure cultures of SRB. The 2% and 3.5% NaCl modified VMNI media contained 0.37 mol L^{-1} and 0.62 mol L^{-1} of chloride ions. VMNI was composed of (g L^{-1} distilled water): NaCl, 20.0; NH_4Cl, 1.0; $CaCl_2 \times 2H_2O$, 0.04; Na_2SO_4, 4.5; $MgSO_4 \times 7H_2O$, 0.06; $FeSO_4 \times 7H_2O$, 0.004; sodium lactate, 6.0; KH_2PO_4, 0.5; sodium citrate, 0.3; casamino acids, 2.0; tryptone, 2.0; modified Wolfe's mineral elixir (0.1% v/v) and vitamin solution (0.2% v/v). The vitamin solution was composed of (g L^{-1} distilled water): riboflavin, 0.1; nicotinic acid, 0.25; thiamine, 0.3; pentatonic acid, 0.3; pyridoxine, 0.3; cyanocobalamin, 0.025; ascorbic acid, 1; biotin, 0.005. The composition of the modified Wolfe's elixir was (g L^{-1} distilled water): Nitrilotriacetic acid, 1,5; $MgSO_4 \times 7H_2O$, 0.06; $MnSO_4 \times H_2O$, 0.5; NaCl, 1; $FeSO_4 \times 7H_2O$, 0.1; $CoSO_4 \times 7H_2O$, 0.1; $NiCl_2 \times 6H_2O$, 0.1; $CuCl_2 \times 2H_2O$, 0.1; $ZnSO_4 \times 7H_2O$, 0.1; $CuSO_4 \times 5H_2O$, 0.01; $AlK(SO_4)_2 \times 12H_2O$, 0.01; H_3BO_3, 0.01; $Na_2MoO_4 \times 2H_2O$, 0.01; $Na_2SeO_3 \times 5H_2O$, 0.001.

G. sulfurreducens ATCC 51573 growth media was prepared following the DSMZ protocol for preparation of DSMZ 826 GEOBACTER [22], and containing 0.05 mol L^{-1} of chloride ions. The DSMZ 826 GEOBACTER media was composed of (in 980 mL of distilled water): NH_4Cl, 1.5 g; Na_2HPO_4, 0.6 g; KCl, 0.1 g; sodium acetate

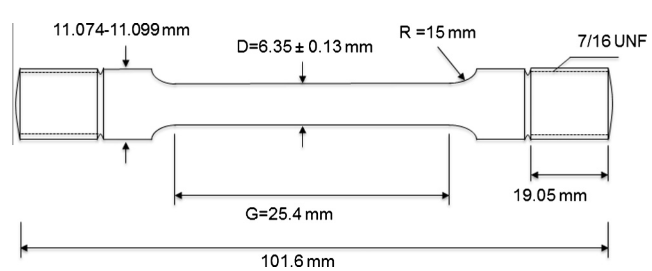

Fig. 1. Characteristics of the tensile specimen fabricated form S235JR carbon steel rod (with a 2 cm diameter).