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Corrosion behavior of X65 steel in seawater containing sulfate reducing bacteria under aerobic conditions

Qiushi Li, Jihui Wang *, Xuteng Xing, Wenbin Hu

Tianjin Key Laboratory of Composite and Functional Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

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ABSTRACT

The corrosion behavior of X65 steel was investigated in the seawater inoculated with sulfate reducing bacteria (SRB) under the aerobic environment by electrochemical impedance techniques and immersion tests. The corroded morphologies and the composition of the corrosion products were investigated. The variation of the solution parameters including the bacterium number, the pH value and the soluble iron concentration were also investigated. The results indicated that in the SRB-containing system, the impedance responses presented a depressed semi-circle in the initial period, which then turned into the blocked electrode characteristic during the later immersion. The biofilm, mainly composed of extracellular polymeric substances, $Fe(OH)_3$, γ-FeOOH and α-Fe_2O_3, formed and degraded with the SRB growth. The soluble iron concentration initially increased, then rapidly decreased and later slowly increased. In the SRB-containing seawater under the aerobic environment, the X65 steel was corroded in the initial immersion. The corrosion became inhibited with the forming of the biofilm during the subsequent immersion. The inhibition efficiency rapidly increased in the logarithmic phase, remained stable in the stationary phase and then decreased in the declination phase. In the corrosion process, the biofilm metabolized by SRB played a key role in the corrosion inhibition of X65 steel.

1. Introduction

Corrosion under the presence of microorganisms has been recognized as a common phenomenon in both natural environments and industrial processes. Microorganisms can be widely found in water environments. Microorganisms tend to attach to the surface of metals and form particular biofilms. This phenomenon changes the physical and chemical properties at the interface between the metal and the solution. These changes of the physical and chemical properties have considerable influence on the corrosion behavior of metals. The corrosion process in the presence of microorganisms is known as microbiologically influenced corrosion (MIC).

Generally, sulfate reducing bacteria (SRB) are considered to be one of the typical microorganisms that can cause MIC, consequently accelerating the corrosion under the anaerobic environment [1–4]. Various researches have been reported to study the influence of SRB on the corrosion behavior of metals [5–7]. The studies of corrosion mechanisms by SRB have been reviewed, including the initial cathodic depolarization theory [8], the anodic depolarization [9], the sulfide-induced stress corrosion cracking [10–12] and the biocatalytic cathodic sulfate reduction (BCSR) theory [13]. Recently, further researches have reported on the electron transfer process based on the BCSR theory [14,15]. Because the iron is insoluble, the electrons released by Fe^0 oxidation are extracellular to SRB cells. To use the extracellular electrons for the sulfate reduction, which happens in the cytoplasm through biocatalysis, a transfer process of the electrons across the cell wall is essential, this is called the extracellular electron transfer (EET) [16,17]. Two types of EET have been reported. One is the direct electron transfer [18–21] and the other is the mediated electron transfer [22]. The two transfer methods explain how the SRB acquires electrons under different conditions. The mechanisms illuminate the way by which SRB accelerate corrosion under anaerobic environment.

Apart from the acceleration effect, SRB can also lead to microbially influenced corrosion inhibition (MICI). Videla et al. have investigated that under anaerobic environment, SRB-induced corrosion can be affected by the conditions of the generated inorganic sulfide derived from the SRB environment. The physical and chemical properties of these sulfides are influenced by environmental parameters. Thin adherent films of sulfide on the surface are protective, while bulky precipitates work inversely, enhancing corrosion rate [23–25]. The possible mechanisms of MICI under anaerobic environment have been discussed by Zuo and Videla in their overview articles [26,27] and it can be achieved in conditions in which (1) corrosive ingredients are removed or hindered from reaching the metal surface, (2) the growth of the corrosion causing bacteria is inhibited by antimicrobials secreted by the

* Corresponding author.
E-mail addresses: qsli@tju.edu.cn (Q. Li), jhwang@tju.edu.cn (J. Wang), wbhu@tju.edu.cn (W. Hu).

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coexisting bacteria present within the biofilm, (3) stable and protective films are formed on the metal surface.

As SRB have always been regarded as a strict anaerobe, most researches have been focused on the effects of SRB on the corrosion behavior of metals under anaerobic environments. Recent studies report that SRB can exist under the aerobic condition because of the gene expression of superoxide dismutase and catalase enzymes [28–32]. Wan et al. have reported that SRB have a slow growth under the aerobic condition [33]. Few studies have reported the effects on the corrosion influenced by SRB under aerobic environments. It is not clear whether the corrosion is accelerated or inhibited by SRB in the presence of oxygen. For a corrosion process under aerobic environment at neutral pH, the oxygen reduction is the dominating reaction at the cathode. This reaction is sensitive to electrode surface conditions and electrolyte environments, which would be affected by the SRB growth. Thus, the influence of bacterial metabolites on the cathodic reduction of oxygen is still an open topic.

In this paper, a corrosion condition in the presence of SRB at neutral pH under the aerobic environment is proposed. The corrosion behavior of X65 steel is investigated under the proposed condition. The abiotic system is used as the contrast test. Electrochemical impedance measurements are conducted to determine whether the corrosion is accelerated or inhibited under the proposed condition. The corroded morphologies of the X65 steel are observed using the scanning electron microscope (SEM). The composition and valence of the corrosion products are determined using the X-ray photoelectron spectroscopy. Furthermore, the evolution of solutions during the experiment are monitored by the most probable number (MPN) method and inductively coupled plasma mass spectrometry. The corrosion mechanism of the X65 steel under the proposed condition is developed based on the comprehensive analysis of electrochemical impedance measurements, surface characterizations and solution evolutions.

2. Materials and methods

2.1. Materials

The chemical composition of the PSL2 X65 steel is shown in Table 1. Coupons with the dimension of 10 mm × 10 mm × 3 mm were cut from a tube sample. The coupons for electrochemical measurements were encapsulated by epoxy resin after welding with copper wires. All coupons were ground by SiC paper up to 1500 grit, then cleaned with ethanol. The ground coupons were then packaged with aluminum foil tightly and sterilized in autoclave at 121 °C for 20 min.

2.2. Culture and media

The SRB strain used in this work was obtained from the Institute of Oceanology, Chinese Academy of Sciences. The SRB strain was isolated from rust layers of carbon steels immersed in Bohai Sea (Qingdao, China). The SRB strain was identified to be a *Desulfovibrio* sp. strain by the comparison of 16S rDNA sequences with the reference strains held in GenBank database. The 16S rRNA gene sequences of the present SRB strain were available in the GenBank database with the accession number of MF461625 [34].

A modified Postgate's culture medium, composed of (per liter of ultrapure water) NaCl 36.27 g, K_2HPO_4 0.65 g, NH_4Cl 1.0 g, $MgSO_4$ 2.0 g, $CaCl_2$ 0.1 g, Na_2SO_4 0.5 g, yeast extract 1.0 g and sodium lactate 4 mL (electron donor), was used for bacterial culture. The pH value of the medium was adjusted between 7.2 and 7.3 by adding the NaOH solution. For sterilization, the medium was autoclaved at 121 °C for 20 min and cooled to room temperature before the experiment.

Table 1
Chemical compositions (wt%) of PSL2 X65.

Alloy	C	Si	Mn	Ni	Cr	Mo	Cu	V	Nb
X65	0.09	0.26	1.30	0.15	0.04	0.17	0.13	0.04	0.03

2.3. Electrochemical measurements

The corrosion behaviors of X65 steel in both the abiotic system and the SRB-containing system were measured by an electrochemical workstation (Autolab 302N, Metrohm, Switzerland) with a three-electrode system. Modified glass cells with the capacity of 300 mL were used for the electrochemical impedance spectroscopy (EIS) measurement. As an abiotic control system, the modified cell was filled with 200 mL sterile medium. As a SRB-containing system, 2 mL SRB seed culture (3 days cultured) was used to inoculate the 198 mL sterile medium to provide an initial bacterium concentration of approximately 1.0×10^5 cfu·mL^{-1}. Two X65 steel coupons were placed in the modified cell. One was served as a working electrode (WE) and the other was for the parallel test. The working area of the WE was 1 cm^2. A platinum plate was used as counter electrode (CE) and an Ag/AgCl electrode (saturated KCl) served as reference electrode (RE). After assembling with corresponding electrodes and coupons, the modified cells were hermetically sealed and placed in an incubator at 30 °C during the whole experiment. EIS measurements were carried out at open-circuit potential (OCP), using a frequency range from 100 kHz to 0.01 Hz and an amplitude of 10 mV. The data were fitted by ZSimpWin software after measurements.

2.4. Surface characterizations

Immersion tests were simultaneously conducted for the surface characterizations and solution analysis. The immersion tests are parallel to the electrochemical measurements. Each immersion test contained two coupons and at each time, two sets of the immersion test were prepared for each condition. Coupons for surface analysis were taken out from immersion after 8 h, 2 days, 5 days and 11 days. The coupons were rinsed by ultrapure water and immersed in an immobile liquid containing 2.5% glutaraldehyde for 1 h in order to immobilize the biofilm. Then, graded dehydration was applied to the coupons with 30, 50, 70, 90 and 100 vol% ethanol (each for 15 min). The whole operation process was conducted on a clean bench.

The surface and cross-sectional morphologies were observed by the scanning electron microscope (SEM, S-4800, Hitachi, Japan) at 5 kV accelerating voltage. The elemental composition and valence of the corrosion products were measured by the energy dispersive spectroscopy (EDS, Genesis XM2, EDAX, USA) at 15 kV accelerating voltage and X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, ULVAC, Japan). C 1s peak at 284.6 eV was set as the reference to correct the shifts.

2.5. Solution analysis

After the coupons were removed from the immersion vessels, the solution in the vessels were shaken and mixed evenly. Three sets of solutions were taken from each vessel to measure the bacterium number, pH and concentration of soluble iron respectively. The number of active SRB in each SRB-containing system was estimated using the most probable number (MPN) method according to ASTM D4412-15 [35]. The pH values for the abiotic system and the SRB-containing system after different time of immersion were measured by a pH meter (PHSJ-4A, Shanghai Electronics Science Instrument, China). The pH measurements were conducted immediately after solutions were taken out of the vessels to reduce the influence of volatilization and oxygen. The concentration of soluble iron for abiotic and SRB-containing systems at different time were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, 7700x, Agilent, USA).