Corrosion of bare and silane-coated mild steel in chloride medium with and without sulphate reducing bacteria

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ARTICLE INFO

ABSTRACT

Influence of Bis[triethoxysilyl]ethane (BTSE) silane coating on the corrosion resistance of a mild steel in an aerobic chloride medium and an anaerobic microbial medium containing sulphate reducing bacteria (SRB) was analysed using a comprehensive electrochemical and chemical analyses. The Silane coating acted as a physical barrier and significantly improved the corrosion resistance of mild steel in an aerobic chloride medium. However, the improvement was limited in the anaerobic microbial medium. Surface morphology examination and chemical analysis using Fourier transformed infrared spectroscopy confirm the formation of a dense biofilm on BTSE-coated surface after pre-exposure to biotic media, which can be attributed to the absence of any antimicrobial functional group in this silane. This study is first of its kind to indicate the limitations of established coating systems in retarding microbial corrosion and emphasizes the importance of the modification of current coating systems with anti-microbial functional groups to impede the formation of biofilms and effectively hinder microbial corrosion.

1. Introduction

Good mechanical properties and the low cost have rendered mild steel to be widely used as a construction material in many industries [1]. However, the use of mild steel is restricted due to their poor corrosion resistance in the marine environment. Their performance is further limited by microbiologically influenced corrosion (MIC) in marine and other corrosive environments. Such limitations often necessitate application of suitable chemical treatments and/or coatings.

Chromate conversion coatings are well known to improve the corrosion resistance of different metals and alloys. However, the carcinogenic nature of hexavalent chromium ions is increasingly restricting application of these coatings, thus necessitating environmentally friendly alternatives. Silane coatings provide significant corrosion protection to metals and alloys and can enhance the compatibility of the metal surfaces with the subsequent paint systems [2]. Furthermore, the cost effectiveness and ease of application of silane coatings render them to be an attractive alternative to the established chromate conversion coatings [3,4].

The general chemical structure of a silane is $X_nSi(CH_2)_mY$, where, X is any hydrolysable alkoxy group and Y is the functional group. The hydrophilicity or hydrophobicity of Y determines the barrier properties of the resultant silane coating [5,6]. Silanes with six hydrolysable groups (X_n; n = 6) are known as bis-silanes. Bis-silanes are well known to develop high densities of metallo-siloxane bonds on the metal substrates as bis-silanes possess greater number of hydrolysable alkoxy groups [7]. Bis[triethoxysilyl]ethane (BTSE) is a typical bis-silane, which has been found to significantly improve the corrosion resistance of various metal and alloy systems [8,9].

Although several investigations have reported the barrier properties of various silane treatments on metals and alloys, only a few [10–12] have provided any insight into the role of these silanes in mitigation of microbial corrosion, which is generally considered as one of the major causes of degradation of various metals and alloys in marine environment. In this study, systematic electrochemical and chemical characterizations have been performed to investigate the influence of BTSE coating on the corrosion resistance of a mild steel in an aerobic chloride medium (0.6 M sodium chloride) as well as in an anaerobic microbial medium (modified Postgate C with and without sulphate reducing bacteria (SRB), Desulfovibrio salexigens bacteria).

2. Experimental procedure

2.1. Silane hydrolysis

Bis-[triethoxysilyl]ethane (BTSE) was procured from Gelest, Inc. The hydrolysis conditions of BTSE have been reported elsewhere [5]. Briefly, 4% (volume%) BTSE, 0.4% acetic acid, 6% water and 89.6% methanol were mixed and stirred for 1 h. The resultant mixture was aged at room temperature for 48 h without any stirring. pH of the resultant solution was measured to be 4.

2.2. Sample preparation and coating procedure

Mild steel (grade 250) strip was cut into rectangular coupons (25 mm × 25 mm × 12 mm). These coupons were ground (up to 2500 grit), degreased with acetone and dried with compressed air.

In order to improve the wettability of the metal substrates, specimens were immersed in 2.5% (w/w) sodium hydroxide (NaOH) solution for 10 min. Subsequently, the coupons were rinsed with deionised water and dried with compressed air. The alkali pre-treated specimens were then immersed in the hydrolysed BTSE solution for 25 min. These specimens were further cured in a conventional oven at 120 °C for 1 h.

2.3. Electrochemical measurements

For electrochemical tests, a copper wire was soldered to each specimen. The wire was encased in a glass tube to prevent any contact of the wire with the electrolyte. The specimens were mounted in a non-conducting resin, with one side (1 cm^2) exposed for electrochemical measurements. In order to prevent crevice corrosion during electrochemical tests, the interfaces between metal and resin were coated with an enamel coating and were left to dry for 12 h in a desiccator. The details of the design of the electrochemical cell and electrochemical tests are provided in the supporting information (Section S1).

Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were carried out using a Princeton Applied Research Potentiostat (model: 2273) and a three-electrode electrochemical cell. The BTSE-coated and uncoated mild steel specimens were used as the working electrodes, saturated calomel electrode (SCE) was used as the reference electrode and a platinum mesh was used as the counter electrode. Preparations of the various test media are described in the supporting information (Sections S1 and S2). All the measurements were repeated at least thrice to examine reproducibility.

Open circuit potential (OCP) was monitored for at least 1 h to confirm its stability with time. A fluctuation of OCP within 10 mV for a period of 1000 s was considered as a stable potential before carrying out the electrochemical measurements [13,14]. Electrochemical impedance spectroscopy (EIS) was performed on all the specimens at different times of immersion in aerobic environment (0.6 M NaCl) and anaerobic environment (modified Postgate C with and without sulphate reducing bacteria, SRB) by applying a sinusoidal potential perturbation (amplitude of 10 mV) at OCP (which the potentiostat kept measuring even during EIS). The impedance was measured at frequencies between 1 MHz and 10 mHz, recording 10 points per decade of frequency using a PAR PowerSuite Electrochemistry package. Impedance analysis was carried out using PAR ZSimpWin package for Windows generally for frequencies between 100 kHz and 50 mHz to prevent misinterpretation of any artefacts that may be present in the high frequency region, or the scatter in the low frequency region. Potentiodynamic polarization was carried out at a scan rate of 0.166 mV/s, starting at a potential of 250 mV more negative to the OCP.

2.4. Scanning electron microscopy

The thickness of the coating and the post corrosion morphology of the BTSE coated specimens in aerobic and anaerobic media were characterized using a JEOL 7001F scanning electron microscope (SEM) operating at 15 keV. To examine the thickness of the BTSE coating the cross section of a BTSE coated specimen was cold mounted and ground with a 2500 grit SiC paper. The sample was subsequently washed with deionized water and ethanol and dried with compressed air. All the specimens were gold coated prior to SEM to avoid charging of the less conductive silane layer.

2.5. Attenuated total reflectance – Fourier transformed infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra, of the residue collected from the biotic medium and the corrosion product film developed on the BTSE-coated specimen pre-exposed to the biotic medium, were collected using a PerkinElmer Spectrum 100 series FTIR spectrometer in the mid-IR range from 4000 to 400 cm^{-1}. For each test, 64 scans were performed with a spectral resolution of 4 cm^{-1}. Background scans were performed prior to the collection of each FTIR spectrum and were subtracted from the collected FTIR spectra.

3. Results and discussion

3.1. Uncoated steel in anaerobic abiotic and biotic environment

Fig. 1a and b show the potentiodynamic polarization plots for uncoated specimens after pre-exposure for different durations (3, 7 and 14 days) to the modified Postgate C medium without and with the bacteria (i.e., the abiotic and biotic media). As seen from Fig. 1a, the pre-exposure to the modified Postgate C media without bacteria (abiotic condition) did not affect the corrosion potential (E_{corr}) or the anodic or cathodic current densities of the uncoated specimens. This behaviour is attributed to the absence of oxygen that can influence corrosion. However, in the case of exposure to the biotic medium (SRB containing anaerobic medium, Fig. 1b), the corrosion potential became more negative (for instance, the potential was 140 mV more negative after 14 days) and the anodic current densities increased at lower overpotentials (< -0.6 V$_{SCE}$). The greater corrosion current density of the steel in the presence of the biotic medium can be attributed to the increase in SRB activities with duration of immersion. The most relevant mechanism in this respect is the utilization of hydrogen and the eventual generation of substantive amounts of cathodic sulphur compounds [15–17]. It is noted that at potential ≥ 0.6 V$_{SCE}$ the anodic current density suddenly started to increase exclusively for the steel pre-immersed in the biotic medium for 14 days (and, not for the steel pre-immersed for 3 and 7 days). This behaviour can be attributed to the considerable increase in generation of large quantities of sulphur compounds but only upon extended exposure of mild steel to SRB-containing chloride for long duration (e.g.; 14 days). Ferrous sulphide (FeS), which is highly cathodic to steel, causes acceleration of corrosion when it is present in amounts insufficient for complete surface coverage. On the other hand, a complete surface coverage by FeS can considerably improve corrosion resistance of steel in chloride solution. Whether or not a continuous layer of FeS will form (and provide protective barrier against corrosion) would depend on the sufficient amounts of both Fe^{+2} and S^{-2} ions to be available. Pre-exposure of mild steel to SRB-containing chloride solutions for different durations, and the subsequent potentiodynamic polarization scans provide an interesting data that illustrate the conducive electrochemical conditions for formation of a FeS layer as well as its robustness. An exposure of mild steel to SRB-containing chloride solution for 14 days produced considerable S^{-2} and Fe^{+2} ions. However, one of them (presumably Fe^{+2}) was not available in sufficient quantity to allow formation of a complete layer of FeS, instead, FeS seems to have formed only sporadically. The presence of FeS islands shifted E_{corr} to more positive direction and caused rapid corrosion. When this sample was subjected to anodic polarization this resulted in rapid generation of sufficient