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Research Article

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Microscopic studies on formation of corrosion product layer on steel exposed to simulated seawater influenced by sulfate-reducing bacteria

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ABSTRACT

Anaerobic bacteria, especially sulfate-reducing bacteria (SRB), play an important role in the corrosion of steel in marine environment. Considering the marine immersion corrosion of mild steel, the present paper presented environmental scanning electron microscopy(ESEM) morphology images and energy dispersive spectroscopy(EDS) elemental analysis to illustrate the formation process of corrosion product layer on the steel surface induced by the metabolism activity of SRB. The results showed that in the accelerated conditions three layers of corrosion product with different composition and configuration were formed step by step on the steel surface. The metamorphosis of the iron in the steel to forms of iron oxide and to iron-sulphur compounds was also involved.

Keywords: Sulfate-reducing bacteria(SRB); Marine corrosion; Environmental scanning electron microscopy (ESEM); Metamorphosis.

INTRODUCTION

Mental corrosion in neutral media in the absence of air is largely biologically influenced, and sulfate-reducing bacteria (SRB), which have been found almost in all anaerobic environment, are mainly responsible for microbiologically influenced corrosion(MIC)[1-3]. Although comprehensive research in terms of biocorrosion mechanism have been controversially discussed in literature [4-9], SRB are commonly considered to play an important role in the global sulfur cycle and involved in up to 50% of the total carbon mineralization process [10].

The geological significance of SRB activity derives from the production of H_2S, resultant from sulfate-reduction. It may subsequently react with Fe^{2+} to form ferrous sulfides. To our present knowledge, in the presence of sulfate reducing bacteria (SRB), the reaction of the iron proceeds according to chemical and electrochemical reactions as follows:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + 2e^- + 2H^+ \quad (1)$$

$$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O \quad (2)$$

$$Fe(OH)_2 + HS^-_{aq} \rightarrow FeS + OH^- + H_2O \quad (3)$$

$$Fe + HS^-_{aq} \rightarrow FeHS^-_{ads} \quad (4)$$

$$FeHS_{ads} \rightarrow FeHS^+_{ads} + 2e^- \quad (5)$$

$$FeHS^+_{ads} \rightarrow Fe^{2+}_{aq} + HS^- \quad (6)$$

$$FeHS^{+}_{ads} \rightarrow FeS_{ads} + H^{+} \quad (7)$$

Thus, metabolism activity of SRB involving the molecular hydrogen, activating enzyme, hydrogenase participates into these catalysis reactions and a series of different ferrous sulfide species, either non-stoichiometric or stoichiometric (e.g. mackinawite, greigite, smythite, pyrrhotite), are finally formed governed by the concentration of sulfide and the pH[11]. A review on the properties of iron sulphide was given by Smith and Miller[12], and a summary of the inter-relationship of the major sulphide products was given by Richard [13].

However, this process will be even more complex if the composition as well as the intermediate transformation process of corrosion product is taken into account. The transformation from iron to iron sulphide species through iron oxide is well documented in the literature [14-18]. An useful compilation by indirect means of the evidence of the iron/sulphur reduction cycle has been given by Little et al[19]. A.L. Neal et al [20] pointed out that ferric (oxyhydr)oxide was the primary form of iron corrosion product and studied the iron sulfides and sulfur species produced at hematite surfaces in the presence of sulfate-reducing bacteria. R. Jeffrey et al [21] presented a sequence of images which appeared to show steps in the metamorphosis of the iron in the steel to forms of iron oxide and to iron-sulphur compounds induced by bacteria. In addition, recent literature[22-24] showed that green rusts (GRs) were found as intermediate products between Fe^{II} hydroxides and Fe^{III} oxyhydroxides in various anoxic environments, which were metastable and readily transformed through oxidation into more stable iron (hydr)oxides, such as goethite, lepidocrocite, ferrihydrite, hematite, magnetite and ferric GRs.

These previous works are of considerable interest and are important for the exposition to follow, while they are not widely applicable taking into account the different aspects of the problem of concern. This study aims to give a formation mechanism of the corrosion product layer which is expected to show how the corrosion products with different configurations and compositions are formed step by step on the steel surface considering the metamorphosis between the corrosion product species. In addition, the work described arises out of a project aimed at better understanding of the complexities of corrosion under marine immersion conditions.

EXPERIMENTAL SECTION

Sulfate-reducing bacteria were isolated from the sea mud in the Huanghai Sea, China, and then enriched and cultivated anaerobically at 37◦C. A modified Postgate's C medium was used for enrichment culture, which contained 0.5g KH_2PO_4, 1g NH_4Cl, 0.06g $CaCl_2 \cdot 6H_2O$, 0.06g $MgSO_4 \cdot 7H_2O$, 6ml 70% sodium lactate, 1g yeast extract, 0.3g sodium citrate in 1 L aged seawater from Qingdao offshore area. The medium was deaerated by purging with high-purity nitrogen for 20 min and autoclaved at 121◦C, then added sterile 0.004 g/L $FeSO_4 \cdot 7H_2O$. 30 ml of the medium were poured into a 50 mL clean serum bottle, prior to inoculation with 5%(v/v) enriched sulfate-reducing bacteria. Then the medium was given anaerobic treatment mentioned above and ready for experiment.

Specimens used for microscopic observation were mild steel (C 0.17, Si 0.073, Mn 0.70, S 0.008, P 0.012) plates with 20 mm × 10 mm × 2 mm in size, specifically to fit easily in the observation chamber without disturbing the corrosion product layer. The surface of the plates were polished with a series of silicon carbide papers, cleaned with ethanol using an ultrasonic cleaner, followed by rinsing with sterile distilled water to remove the contamination. Then the specimens were kept in a sterile and oxygen-isolated environment, and sterilized by ultraviolet lamp for 30min before next step, insuring of no contamination by other bacteria.

Specimens were exposed to modified medium mentioned above inoculated rich SRB in serum bottles and sealed with cover and paraffin for different immersion time from 7d to 28d at a constant temperature of 37°C. Following incubation, samples with associated precipitates were dispersed in an ultrasonic cleaner, removed from the culture medium and observed using Phillip XL30 ESEM. The morphological changes of the corrosion product were interpreted from analyses made using EDS.

RESULTS AND DISCUSSION

Morphology observation and element analysis of representative corrosion products of mild steel immersed in SRB media after 7, 14 and 28 d are shown in Figs.1~3.

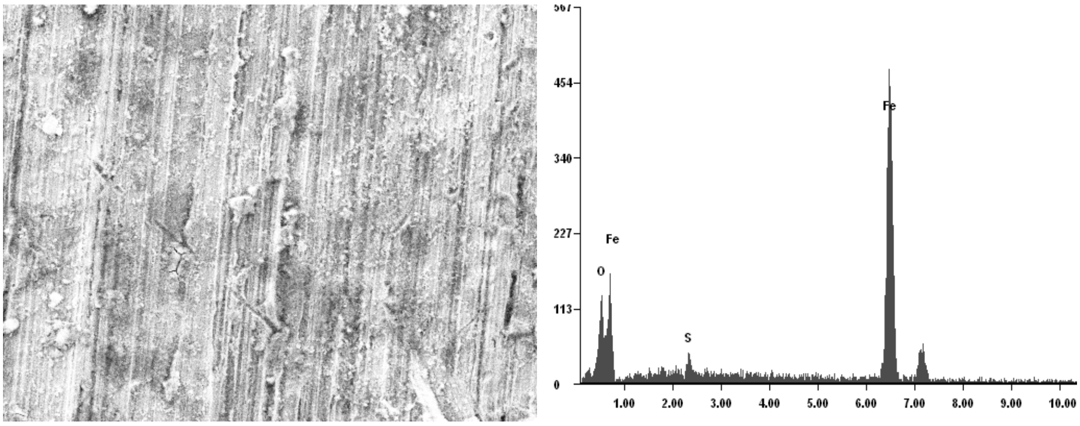


Fig. 1 Surface morphology and element analysis of mild steel immersed in SRB media after 7 d

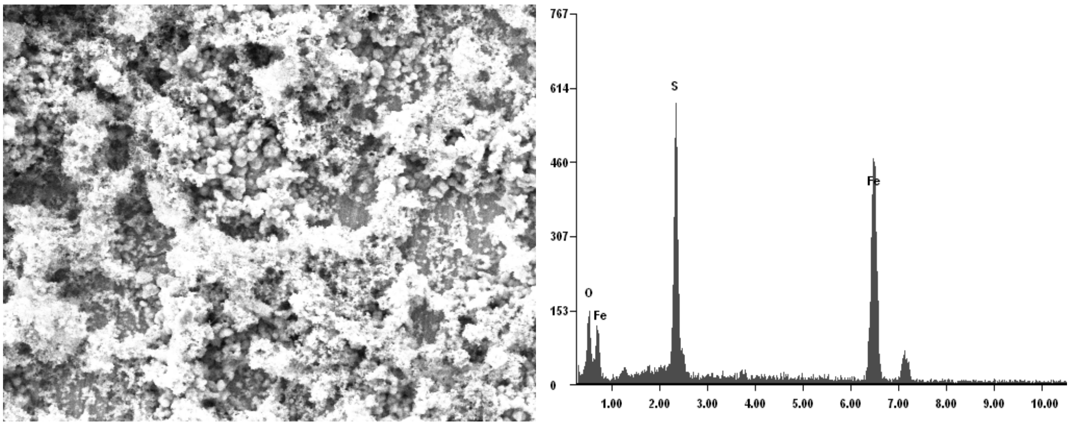


Fig. 2 Surface morphology and element analysis of mild steel immersed in SRB media after 14 d

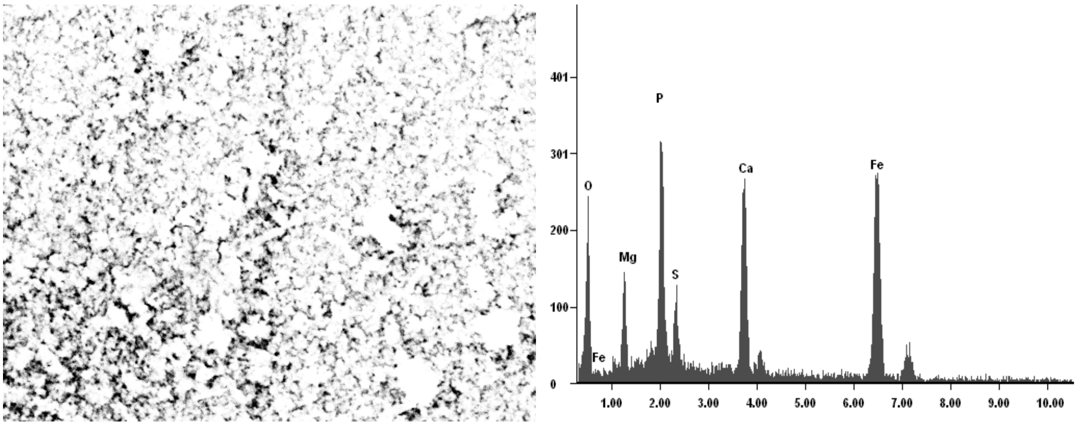


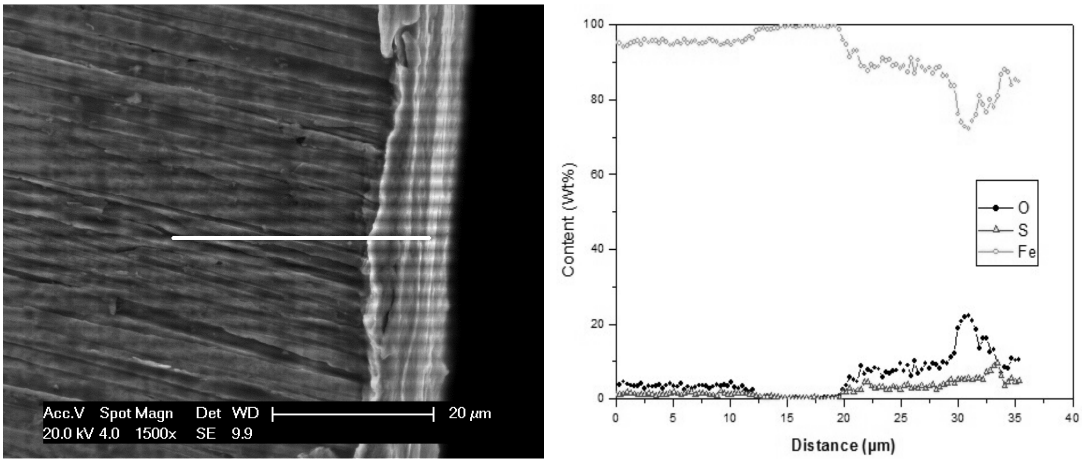
Fig. 3 Surface morphology and element analysis of mild steel immersed in SRB media after 28 d

Specimens had comparatively smooth surface with a thin layer of precipitation and a few attachments after 7 d immersion. Biological identification was not included in this study, but according to the main element analysis of Fe (87.15, wt%), S(2.20, wt%), O(10.65, wt%), typically these plates exhibited certain amounts of iron (hydro)xide after one week. The EDS also indicated little counts of sulphur, which confirmed the presence of sulphur in the corrosion product even at early stage of immersion.

The steel plates were covered with a heterogeneous and thick layer of corrosion and metabolic products after two weeks. An EDS quantitative analysis showed the high content of element sulphur (24.02, wt%) and oxygen(12.49, wt%), indicating the presence of iron (hydro)oxide, sulfide or sulfate. With observation at high magnification, typical globular iron oxide morphology was showed in the inner layer, which was supposed to be iron oxide hydrate ($Fe_2O_3 . H_2O$) and the γ-FeOOH form of hydrated ferric oxide. These iron oxide spheres, as also detected by R. Jeffrey[21] and C. Verati[25], were considered as the primary form of iron corrosion product, and with bacterial induced degradation they were assumed to transform to the spongy globules and strings(in the outer layer, Fig.2) of iron sulphur compounds.

A thick layer of corrosion product was gradually formed on the surface of the specimen immersed for 28 d (Fig. 3). The steel substrate could hardly be seen but the rust layer seemed loose and porous. EDS analysis revealed the presence of element Ca (13.65, wt%), Mg (8.00, wt%), P (13.09, wt%), the common elements in seawater, while content of S(4.20, wt%) decreased comparatively. The loose and porous configuration by the precipitation of carbonates, such as GRs(iron carbonate hydroxide), was formed on the surface of the steel specimen, which was not supposed to provide protective barrier for the steel from the corrosion media.

Elemental line scans were conducted on the cross section of the specimen after 28d immersion subsequently (Fig. 4). As shown in Fig. 4(b), content(wt%) of element Fe, S, O was investigated along the central line in Fig. 4(a) crossing the steel substrate and layer of corrosion products. In the substrate zone the contents were rather stable. While a high peak of element oxygen was found in the inner layer of the corrosion product, with a simultaneous drop of iron and declined afterwards. Another obvious peak showed up almost in the outer layer of corrosion product, which revealed the increase of element sulphur. In general, element oxygen was rich in the inner layer of corrosion product and element sulphur was rich in the outer layer. It was indicated that oxygen-rich iron (hydro)xide, emerged at the early stage of corrosion as the primary corrosion product. With influence of the metabolic activity of microbes, the iron (hydro)xide especially in the outer position exposed to the SRB media transformed to the sulfur-rich product. Referring to the above results, the subsequent precipitation of element Ca, Mg, P after long exposure time resulted in the comparative decrease of element O and S in the very surface layer finally. It was in good accordance with the above results and deduction.



(a) **(b)**

Fig. 4 Elemental line scans on cross section of mild steel immersed in SRB media after 28 d

Steps of MIC induced metamorphosis of the iron corrosion products were well documented with various techniques for different steels exposed to natural or simulated seawater conditions. The corrosion products were known to be an extremely complex mixture of sulphides, oxides and carbonates with the influence of various parameters such as the pH, concentration of certain ions, temperature, bacteria species and so on.

Different from the previous work, this study herein focused on the transformation process as well as the formation of corrosion product layer in simulated marine immersion corrosion of mild steel under well controlled experimental condition. It was known that the role of anaerobic bacteria in the marine corrosion of steels appeared to be particularly important for higher water temperatures and longer durations as then anaerobic conditions appeared to govern[26]. Temperature controlled at 37°C in the present study favored the proliferation of the bacteria, thus facilitated the metamorphosis process and formation of the corrosion product layer and accelerated it. Then the formation mechanism of inner and outer layer, strictly speaking, three layers of corrosion products were presented: the first layer was mainly composed of iron oxides, the primary corrosion products; the second layer was composed of iron sulphides(or polysulphides), the metamorphosis product from the iron oxides by bacterial induced degradation; the third layer consisted of precipitation of calcium and magnesium carbonates, formed even after the growth cycle of microbes.

CONCLUSION

By ESEM and EDS techniques, metamorphosis of the iron corrosion product from iron to iron sulphide species through iron oxide as well as the formation mechanism of corrosion product layer in simulated marine immersion corrosion of mild steel was investigated in this study. The constant temperature acceleration experiment presented the general steps of formation of three layers of the corrosion products: iron oxide layer, iron sulphide layer and carbonate layer.

The typical morphology images of iron oxide and iron sulphide showed what appeared to be details of the involvement of bacteria in the metamorphosis and EDS elemental analysis at interval immersion period together with the line scan results provided evidence for the formation kinetics of corrosion products. Although the work was conducted in a simulated condition, it was also expected to be adoptable for the explanation of corrosion mechanism in natural marine environment.

Acknowledgements

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