



Effect of microstructure on sulfide scale formation and corrosion behavior of pressure vessel steel in sour environment



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ABSTRACT

To elucidate the influence of steel microstructure on sulfide scale (FeS_x) formation and corrosion behavior of pressure vessel steel in sour environment, two kinds of microstructure of ferrite/pearlite and bainite are evaluated. This study clearly reveals that the morphology of sulfide film formed on the steel is remarkably similar to that of the microstructure of the steel substrate, and sulfide film is preferentially precipitated on the cementite (Fe_3C) and pearlite with low hydrogen overvoltage and acts as a cathode with respect to ferrite. Moreover, it is evident from electrochemical corrosion evaluation that measured current density of bainite is higher than that of ferrite/pearlite, and the polarization resistance is the other way around, suggesting that, it could be easier for aggressive ionic species to be penetrated into the sulfide film formed on the steel substrate with bainite. The precipitation property of sulfide scale depends greatly on the steel microstructure characterized by the distribution of Fe_3C , which in turn has an influence on the corrosion behavior within a given specific period of 72 h. The differences in the shapes and distributions of Fe_3C could affect the mechanical attachment of the sulfide scale with the steel substrate. Long range of Fe_3C network of pearlitic grains could promote better adhesion of the scale for the steel with ferrite/pearlite, while much finer Fe_3C particles of the bainitic microstructure could lead to easy detachment of the scale from the steel with bainite.

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1. Introduction

The corrosion of pressure vessel steel used in oil and gas field applications has been of great concern for metallurgists and corrosion engineers [1–3]. From the current knowledge of aqueous sour corrosion, it is generally accepted that the corrosion occurs in the form of electrochemical reactions on the steel surface. The corrosion reaction includes the anodic steel dissolution ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) and the cathodic hydrogen reduction ($\text{H}^+ + \text{e}^- \rightarrow \text{H}$). Particularly, major environmental corrosive species in this field are the sweet and sour gases dissolved in the ever present brine. In general, CO_2 is present at higher concentration, and it makes the environment acidic [4,5]. In the case of the H_2S , the corrosion behavior can be controlled mostly by precipitation of corrosion products on the steel surface. The dissolved Fe cation (Fe^{2+}) reacts with the environmental sulfide species (S^{2-}) dissociated from the H_2S gas, and precipitates to form FeS_x , a corrosion product, which in turn may either accelerate or suppress corrosion of steel under different metallurgical and environmental conditions [6]. In particular, at the higher pH value above 3, the sulfide film can be precipitated on the steel

surface in the form of mackinawite (FeS_{1-x}) by the following reactions [7–9].



It is well established that one of the important factors to control the corrosion rate of the steel in sour environment is to modify the chemical composition of the steel. The effect of various alloying elements such as Cr, Cu and Ni has been reported [10–12]. In particular, above pH 4, the alloying element of Cu has a beneficial effect on the sour corrosion by the formation of a protective film of the type $(\text{Fe}\cdot\text{Cu})\cdot\text{S}$ on the steel surface, which suppresses the hydrogen reduction reaction [12–16]. Our previous investigation [10] has also indicated that the sulfide film

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formed on the surface of Cu and Ni bearing steel shows protective nature with smaller cracks and defects, suppressing effectively both anodic steel dissolution and reduction of proton (H^+).

In general, to achieve further enhancement of mechanical properties, lots of efforts have been directed to optimize the microstructure of the steel. Recently, optimization of steel microstructure has also been motivated by enhancing corrosion resistance, and the corrosion behavior of the steel with a variety of microstructures ranging from ferrite/pearlite to martensite has been evaluated [17–19]. Most researchers assume that the microstructure has an influence only on the corrosion behavior of bare steel, and thus the corrosion behavior after the steel surface is covered by corrosion products of FeS_x has not been clearly investigated. However, our preliminary study has revealed that the microstructure affects significantly the morphology of FeS_x formed on the steel substrate and subsequent corrosion behavior of the steel. Particularly, the formation mechanism of FeS_x film on the steel surface could be closely associated with the distribution of cementite (Fe_3C) in the microstructure. For better understanding of sour corrosion mechanism, there is strong interest to further investigate the relationship among the microstructure characterized by the distribution of cementite, formation behavior of sulfide scale and subsequent corrosion behavior.

In the present study, two kinds of microstructure of ferrite/pearlite and bainite were obtained by controlling the cooling rate in normalizing heat treatment. Their electrochemical corrosion behaviors were studied by means of polarization and impedance technique, and they are compared in terms of formation characteristics of sulfide scale depending on the microstructure of the steel.

2. Experimental

2.1. Specimen preparations and microstructure analysis

The tested material used in this study is a sour-resistant ferritic steel equivalent to ASTM A516 grade pressure vessel steel containing 0.2 wt.% C. The detailed chemical composition of the steel can be found in Table 1. The steel was normalized by heating to 910 °C for 30 min and subsequently cooled to room temperature. To obtain two kinds of microstructure, the cooling rate in the normalizing was controlled with 0.67 °C s⁻¹ (air cooling) and 13 °C s⁻¹ (water quenching), respectively.

For microstructure analysis, the test specimens were initially ground to 2000 grit paper and polished with 0.25 μm diamond suspension. The specimens were then degreased with ethanol with 5% nital solution. The microstructure was examined with optical microscope (OM) and field emission-scanning electron microscope (FE-SEM). Moreover, the morphology of iron sulfide scale precipitated on the tested steels after immersing in the H₂S-saturated NACE TM0284-96A solution [20] for 24 h was also examined using FE-SEM.

2.2. Electrochemical corrosion tests

The electrochemical corrosion tests employed in the present study include the potentiodynamic and potentiostatic polarization, and electrochemical impedance spectroscopy (EIS) measurements. For these electrochemical tests, the platinum foil, saturated calomel electrode (SCE) and specimens were used as counter, reference and working electrode, respectively. Particularly, in this study, to evaluate

the influence of sulfide scale formed on the tested steels with different microstructures on the corrosion resistance, the specimens were initially immersed in the H₂S saturated NACE solution [20] for certain periods before the electrochemical corrosion tests were conducted. During the electrochemical experiments, there was no stirring in the test solution and basically, the conditions were stagnant.

Firstly, for the potentiodynamic polarization measurement, a potential was applied and scanned potentiodynamically at a scan rate of 0.16 mV s⁻¹ from an initial potential of -150 mV to 150 mV versus open circuit potential (OCP). The measurement was conducted after 24 h and 72 h immersion.

Secondly, to identify the difference in polarization resistance between the two microstructures, depending on the formation characteristics of sulfide scale on the steel surface, the impedance test was conducted at OCP, applying a 10 mV amplitude sinusoidal voltage in 0.01–100,000 Hz frequency interval. The EIS measurement was also performed on the steel after the surface of steel was covered by the sulfide scale, and the measurement was conducted after 24 h and 50 h immersion.

Thirdly, for the potentiostatic polarization measurement, a constant potential of 50 mV above OCP, which has been an effective potential value to analyze the properties of the sulfide film formed on the ferritic steel in acid sour environment [10], was applied on the steel, and the change in the current density was recorded. In fact, the major goal of the potentiostatic polarization measurement is not to provide severe environment but to simulate actual environment by applying a small anodic overpotential slightly higher (+30–50 mV_{sce}) from its OCP, and obtain the electrochemical signal (i.e. change in current density) with the immersion time. Based on the change in current density under the constant anodic overpotential, it is possible to gain further insight into the stability of corrosion scale on the steel surface, and to evaluate the anodic dissolution rate of the steel with the immersion time.

2.3. Analysis on iron sulfide film

To identify the composition of sulfide film as a function of depth, glow discharge spectroscopy (GDS) was utilized. The surface was analyzed after the steel surface was covered by the sulfide film by immersing in the NACE solution for 24 h, like the case of the electrochemical corrosion test. One of the difficulties when analyzing iron sulfide films is the high reactivity with oxygen. In order to keep out oxygen from the specimen removed from the test solution, the specimen was stored in oxygen free desiccator until the onset of measurement. Although it is impossible to completely block out oxygen from the specimen, this treatment can contribute to the minimization of the exposure to oxygen before the measurement.

In addition, to observe the cross-sectional view, focused ion beam (FIB) was employed. Prior to the cross-sectional observation by ion beam induced secondary electron image, the protection layer using carbon deposition with 1 μm thickness was applied on the sulfide film formed on the steel surface to protect the sulfide film from the damage by the ion beam.

3. Results and discussion

3.1. Microstructure observation

Fig. 1 presents the microstructure of the two tested steels obtained by two kinds of cooling rate in normalizing heat treatment. Fig. 1(a) exhibits the microstructure consisting of typical ferrite/banded pearlite with an average grain size of 17 μm. The inset figure indicating the magnified view of the microstructure shows clearly the morphology of pearlite composed of alternating layer of ferrite and cementite (Fe_3C). Fig. 1(b) exhibits the microstructure consisting of bainite with small amount of ferrite. The inset figure shows the bainite lath with fine carbide particles (Fe_3C) distributed along the lath boundary.

Table 1
Chemical composition (wt.%) of the tested steel.

Chemical composition (wt.%)									
C	Mn	P	S	Al	Ti + Nb	Cu	Ni	Cr + Mo	
0.15–0.2	1.0–1.2	0.003	<0.002	0.04	0.03	0.221	0.339	0.03	

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