

## Characteristics of Oxide Films Formed on A106 Gr.B and A335 P22 in a Flowing Alkaline Solution at 150 °C

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### 1. Introduction

Carbon steels have used as pipeline materials in both fuel power plants and nuclear power plants in worldwide. However, carbon steel pipelines have been frequently damaged by the flow-accelerated corrosion (FAC), leading to an economic loss as well as human accidents [1]. Therefore, many studies have conducted to improve the FAC resistance of carbon steels. Results have validated that the addition of Cr, Cu, and Mo as alloying elements has a positive effect in increasing the FAC resistance. In this regard, pipelines where FAC severely occurs have been replaced with low alloy steels containing Cr, Cu, and Mo. Consequently, the occurrence of FAC was mitigated [2].

FAC behavior is typically affected by the properties of the oxide film formed on the pipeline inner surfaces. Therefore, it is necessary to investigate oxide films formed on carbon steels and low alloy steels under the flowing condition in order to understand the difference in corrosion behavior between these two steels. In this study, the oxide films of A106 Gr.B and A335 P22 were formed under the flowing condition at 150 °C. After that, oxide films were investigated in terms of thermodynamics, dissolution kinetics, and defect properties.

### 2. Experimental Methods

#### 2.1 FAC tests

Test specimens were machined from pipes into a plate shape. FAC test was carried out using a single-phase water circulating loop system at 150 °C for 500 h. The test solution was prepared to have a pH value of 9.0 at 25 °C by adding the ammonium hydroxide in the deionized water. Dissolved oxygen concentration was maintained below 5 ppb by sparging N<sub>2</sub> gas. When test solution reached the target temperature, specimens were rotated so that the linear velocity at the surface of specimens was 5 m/s until the end of the test. The corrosion rates of the specimens were calculated using the weight changes of the specimens before and after the FAC test.

#### 2.2 Characterization of the oxide films

The morphological properties of oxide films were observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The chemical compositions of the oxide films were analyzed using energy dispersive spectroscopy (EDS) attached to a transmission electron microscope. Electrochemical properties of oxide films were investigated through Mott-Schottky plots at 25 °C. The thermodynamic calculation of oxide film formation reactions was conducted using the HSC Chemistry 6 software [3].

### 3. Results and Discussion

Fig. 1 shows the cross-sectional TEM images in the bright field mode and EDS point analysis results of oxide films formed on A106 Gr.B and A335 P22, respectively. The oxide film formed on A106 Gr.B was thick and porous than that formed on A335 P22. The chemical composition of the oxide film formed on A106 Gr.B corresponded to magnetite. Whereas, the oxide film formed on A335 P22 was compact and composed of iron oxide with some amount of Cr.

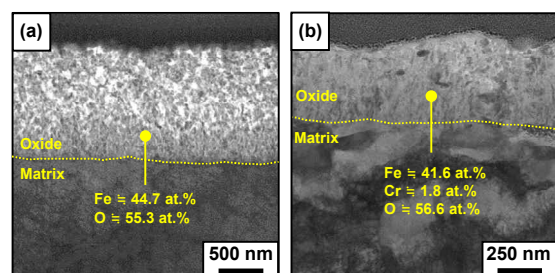
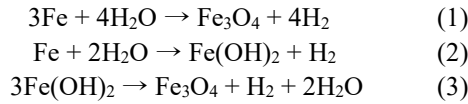
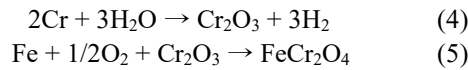


Fig. 1. Cross-sectional TEM images and EDS point results of the oxide films formed on (a) A106 Gr.B and (b) A335 P22 after the FAC tests.

Based on the E-pH diagram of Fe-H<sub>2</sub>O and Fe-Cr-H<sub>2</sub>O systems at 150 °C [4], the formation of magnetite and iron chromite are thermodynamically favored in wide pH and potential regions under the typical secondary water conditions, respectively. Magnetite film can be formed on carbon steels by the following reactions (1) to (3). The Gibbs free energy of reactions at 150 °C yields -99.8 kJ/mol for reaction (1), -22.9 kJ/mol for reaction (2), and -30.9 kJ/mol for reaction (3), respectively.



On the other hand, iron chromite oxide film can be formed by the following reactions (4) and (5). The Gibbs free energy of reactions at 150 °C yields  $-367.1$  kJ/mol for reaction (4) and  $-293.8$  kJ/mol for reaction (5), respectively. This indicates that iron chromite can be more preferentially formed than magnetite on the low alloy steels in the FAC occurrence environment.



Nevertheless, no matter how thermodynamically stable an oxide film is formed on the surface of pipelines, the FAC rate unavoidably increases if this oxide film readily dissolves. Fig. 2 shows the solubility values of magnetite and iron chromite at 100 °C and 200 °C, respectively [5]. The solubility of two oxide films showed similar values in a high alkaline condition due to their thermodynamics properties. However, under the FAC test conditions, the solubility of magnetite is higher by about  $10^3$ -times and  $10^2$ -times than that of iron chromite at 100 °C and 200 °C at each pH condition, respectively. This indicates that the magnetite film has a much faster dissolution rate than iron chromite.

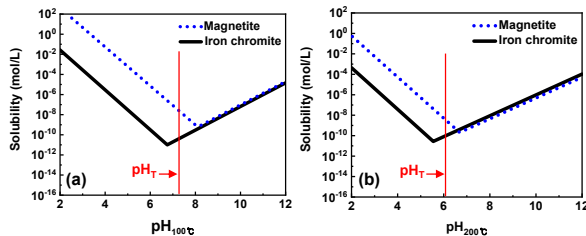


Fig. 2. Solubility values of magnetite and iron chromite at the different temperature: (a) 100 °C, (b) 200 °C [5].

Fig. 3 shows the Mott-Schottky plots of oxide films formed on A106 Gr.B and A335 P22 during the FAC tests. The capacitance responses of the oxide films showed a positive slope in region I, II and a negative slope in region III, indicating an n-type and a p-type semiconductor behavior, respectively.

The total charge carrier densities of the oxide films were calculated using the linear slopes of the Mott-Schottky plots. The charge carrier density of oxide film formed on A106 Gr.B was approximately 124-times higher than that of the oxide film formed on A335 P22. This indicates that the oxide film formed on A106 Gr.B contains a greater point defect density that carries the charge through the films. Since point defects can act as migration paths for metal cations or oxygen ions, A106 Gr.B can be more susceptible to FAC.

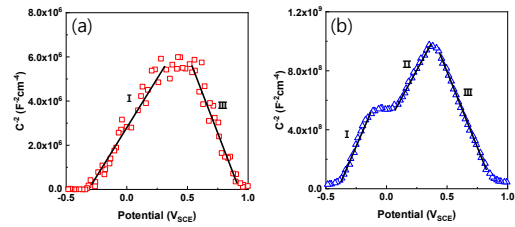


Fig. 3. Mott-Schottky plots of oxide films after the FAC tests: (a) A106 Gr.B, (b) A335 P22.

Table I: Total charge carrier densities of oxide films

Material	Total charge carrier density ( $\text{cm}^{-3}$ )
A106 Gr.B	$7.2 \times 10^{23}$
A335 P22	$5.8 \times 10^{21}$

#### 4. Conclusions

The corrosion behavior of A106 Gr.B and A335 P22 under the flowing condition was investigated in terms of oxide film properties, and the obtained conclusions were as follows.

(1) A porous magnetite film was formed on A106 Gr.B, whereas a compact iron oxide film containing with some Cr was formed on A335 P22. A porous oxide film can act as a macroscopic defect to increase the corrosion rate.

(2) The formation of iron chromite is thermodynamically favored compared to that of magnetite, based on the Gibbs free energy of formation at 150 °C.

(3) The solubility of magnetite was significantly higher than that of iron chromite in the operating conditions of the pressurized water reactor of secondary systems, indicating a higher dissolution kinetics.

(4) The point defect density of oxide film formed on A106 Gr.B was significantly higher than that of the A335 P22. Therefore, corrosion rate of A106 Gr.B can be further accelerated by the microscopically defective oxide film.

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