

Alloying Effect of Mo in Martensitic Stainless Steel on Passive Film in H₂S-CO₂ Environment

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ABSTRACT

13Cr martensitic stainless steel is widely used in oil and gas industry. It is well known that addition of molybdenum (Mo) enhances the passivity of steel. However, the role of Mo in passive film has not been clarified completely. The aim of the present research was to reveal role of Mo in terms of semi-conductivity. The Mott–Schottky plot, obtained by impedance spectroscopy, revealed the effect of Mo addition on the semiconducting property of a passive film under an H₂S environment in a pH 4.0 solution at 25 °C. The results revealed that Cr-O of the inner film and sulfide of the outer film exhibited semiconductor p-type and n-type characteristics, respectively. The number of defects in the film on 2.5 mass% Mo-added steel was approximately half of that in the film on Mo free steel. The role of Mo was discussed through investigation using X-ray photoelectron spectrometric analysis based on the existent state of the passive films.

Key words: Martensitic Stainless Steels, Sour environment, Corrosion mechanisms, Molybdenum, Thin films, Electrochemistry

INTRODUCTION

Oil and gas wells are highly corrosive environments because they contain H₂S and CO₂. The 13Cr martensitic stainless steel is widely used in the oil and gas industry because of high good corrosion resistance in CO₂ gas wells. Generally, the addition of Mo increases the passivity of steel. However, the role of Mo in passive films has not been completely clarified.

The role of Mo was investigated not only in H₂S but also in N₂, such as deaerated seawater. An inhibition effect of molybdate was proposed, since it is insoluble and can prevent metastable pit formation and growth.¹⁻⁶ The effect of molybdate ions (MoO₄²⁻) as inhibitor was considered in understanding the role of alloyed Mo in H₂S environments, and it was reported that it improved the resistance to corrosion pitting.⁷⁻⁸ Contrarily, Ueda and Kudo have proposed a role of alloyed Mo in H₂S environments, which differed from that in non-sour environments; they have also proposed that stable Mo sulfide enhances the formation of a protective chromium oxide film differentiated between sour and non-sour environments, indicating that stable Mo sulfide formation is enhanced.⁹ Furthermore, there is no unified view on the effect of Mo, and its role remains unclear, especially in H₂S-CO₂ environments.¹⁰⁻¹²

Double layer film analysis was performed through semiconductor analysis, and the role of Mo in martensitic stainless steel under H₂S condition was investigated.

EXPERIMENTAL PROCEDURE

Materials

Table 1 lists the main chemical components of the lab-melted materials. Ingot was prepared by vacuum induction melting (VIM), and each steel plate, with a strength of 110 ksi (= 758 MPa) grade, was obtained by hot forging, hot rolling, quenching, and tempering. Each steel plate was machined, polished on one side (the immersion surface) with SiC paper (#600), ultrasonically cleaned with acetone, and subjected to the electrochemical tests.

The microstructures of the samples are shown in Figure 1. All samples had a fully martensitic microstructure.

Table 1: Chemical composition of the lab-melted test specimens (mass%)

Mark	C	Ni	Cr	Mo
Base	0.01	6.0	12.0	<0.01
1.0Mo	0.01	6.0	12.0	1.0
2.5Mo	0.01	6.0	12.0	2.5

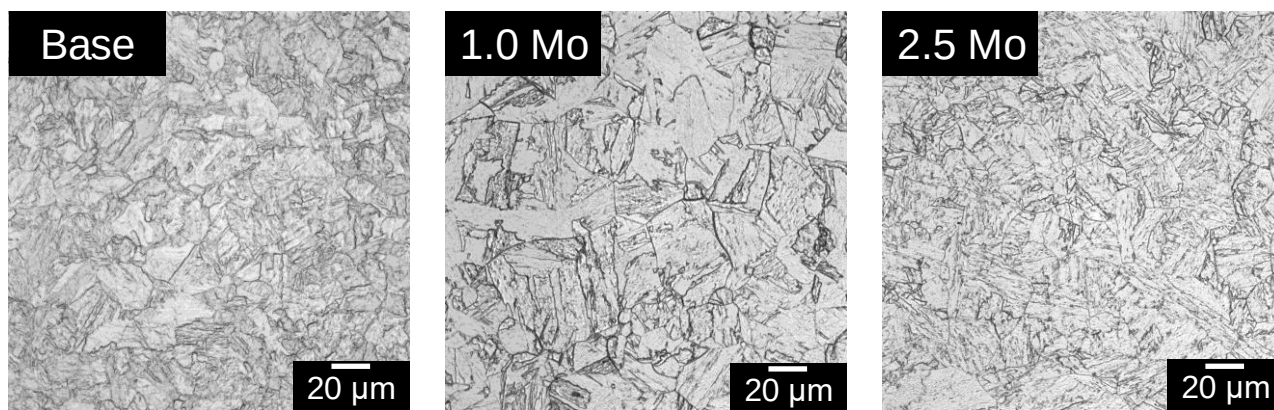


Figure 1: Microstructure of test samples

Test solution

The test solution pH was set to 4.0, by adding acetic acid to 5 mM sodium acetate solution (no Cl^-). The solution was deaerated with Ar gas for over 1 h (flow rate: 200 mL/min for 800 mL solution), followed by saturation with a 10% H_2S - CO_2 bal. gas mixture for over 30 min.

Electrochemical measurement

EnergyLab XM[†] by Solartron analytical was used for the electrochemical measurements. A glass cell, equipped with a platinum sheet counter electrode and a saturated calomel electrode (SCE) as the reference electrode, containing 800 mL of solution was used for the test. The test specimens were fixed with a holder made of PTFE and sealed with a spacer. The polished side was exposed to the solution with an exposure area of 1.0 cm². Test specimens were cathodically polarized for 10 min at -1.0 V (vs. SCE, hereafter V_{SCE}) to remove the air-formed oxide film before each measurement.

For the anodic polarization curve measurement, the electrochemical potential was swept with 0.33 mV/sec. (20 mV/min.) from -1.0 V_{SCE} to 0.5 V_{SCE} at 24 °C. Based on the results from the polarization curve, constant potential polarization was performed for 1 h at the anodic polarization potential (-0.2 V_{SCE}), where the current density was the lowest in the passive current region, and subsequent tests were performed thereafter.

For the alternating current (AC) impedance measurements, an AC amplitude of 10 mV was applied at a frequency range from 100 kHz to 0.01 Hz at -0.2 V_{SCE} as V_{DC} .

The AC impedance was measured at a frequency of 1 Hz for capacitance measurements to estimate the semiconducting properties of the passive film. An electrochemical cell was placed in an incubator, maintained at a constant temperature of 24 °C, and measurements were performed in a dark room to mitigate the effects of changes in visible light and temperature.

XPS depth direction analysis

To estimate the oxide and sulfide composition of the film under constant potential conditions, X-ray photoelectron spectroscopy (XPS) was performed (ULVAC-PHI, Versa Probe III)[†] with an Al $K\alpha$ X-ray (1486.6 eV) source. Ar⁺ sputtering (1 kV) was used to obtain the depth profile.

Non-destructive and quantitative film analysis

The structure of the oxide film was analyzed by X-ray photoelectron spectroscopy (XPS) using an Al $K\alpha$ X-ray source. The XPS spectra were measured in a conventional ultrahigh vacuum (UHV) chamber at beam line 7 B (BL-7B) of New Subaru. New Subaru is the main facility of the Laboratory of Advanced Science and Technology for Industry (LASTI) at the University of Hyogo. The photon energy of the irradiated X-ray was 1487 eV, and the beam spot on the sample was 3 mm in diameter. The angle of the incidence on the X-rays and the detection angle of the photoelectrons were 45 ° from the sample surface. XPS was performed using a VG Scienta XPS spectrometer (R3000)[†].

The binding energy of the spectra, which was recorded using the Al $K\alpha$ line, was experimentally calibrated with the position of the $\text{Au}_{4f-7/2}$ peak, and the spectrum level of the Au film was displayed under UHV. All the XPS spectra were obtained under the same measuring conditions. Photoelectron intensity was normalized with the number of measurements.

RESULTS AND DISCUSSION

Polarization curve Test results

Figure 2 reveals the polarization curves at pH 4.0, with no Cl^- solution. The anodic current density decreases as the Mo content increases, and the peak current density (inset figure) of active dissolution decreases to approximately 10 $\mu\text{A}/\text{cm}^2$ as the Mo content increases to 2.5%. In the passive region (-0.4~-0.2 V_{SCE}), the lowest current density was reduced to approximately half that of the base steel. These results confirmed that the addition of Mo inhibited the corrosion.