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Corrosion Science

Role of alloyed molybdenum on corrosion resistance of austenitic Ni–Cr–Mo–Fe alloys in H_2S–Cl^- environments

Akiko Tomio [a,*], Masayuki Sagara [a], Takashi Doi [a], Hisashi Amaya [b], Nobuo Otsuka [c], Takeo Kudo [d]

[a] Technical Research & Development Bureau, Nippon Steel & Sumitomo Metal Corporation, 1-8 Fuso-Cho, Amagasaki, Hyogo 660-0891, Japan
[b] Nippon Steel & Sumitomo Metal Corporation, Wakayama Works, 1850 Minato, Wakayama City, Wakayama 640-8555, Japan
[c] Nippon Steel & Sumikin Technology Co., Ltd., 1-8 Fuso-Cho, Amagasaki, Hyogo 660-0891, Japan
[d] Former Graduate School of Engineering, University of Hyogo, 2167 Shosha Himeji, Hyogo 671-2201, Japan

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ABSTRACT

Corrosion test and surface analysis were conducted in the H_2S–Cl^- environments to elucidate the role of alloyed molybdenum on the corrosion resistance of Ni–Cr–Mo–Fe alloys. The alloyed molybdenum improves the localized corrosion resistance. The surface film is of double layers which comprise sulfide including molybdenum and chromium oxide. However, the Ni–Mo–Fe alloy also shows good corrosion resistance in the H_2S–Cl^- environment. This good corrosion resistance is considered to be due to the cation selectivity of molybdenum sulfide, which can form in such environments. The role of alloyed molybdenum on the corrosion resistance of Ni–Cr–Mo–Fe alloys in H_2S–Cl^- environments is proposed.

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1. Introduction

Oil and gas wells are very corrosive environments because of a high level of chloride ions and high partial pressures of hydrogen sulfide (H_2S) and carbon dioxide (CO_2). Austenitic Ni–Cr–Mo–Fe alloys have been used in oil and gas wells to obtain high corrosion resistance in H_2S–Cl^- environments and various Ni–Cr–Mo–Fe alloys have been developed [1–10]. Effects of alloyed elements on localized corrosion resistance such as pitting corrosion and stress corrosion cracking (SCC) of Ni–Cr–Mo–Fe alloys in H_2S–Cl^- environments have been investigated and some effective elements have been determined: Ni, Cr, and Mo [11–20]. In particular, the alloyed molybdenum increases remarkably the corrosion resistance of Ni–Cr–Mo–Fe alloys in H_2S–Cl^- environments. For example, Uesugi et al. have reported that the alloyed molybdenum increased the crevice corrosion resistance of duplex stainless steels in the H_2S–Cl^- environment [11]. Ikeda et al. have reported that the alloyed molybdenum increased the corrosion resistance of austenitic Ni–Cr–Mo–Fe alloys in the H_2S–Cl^- environment [12].

The role of alloyed molybdenum has been widely investigated because the alloyed molybdenum can increase the corrosion resistance of austenitic stainless steels and Ni–Cr–Mo–Fe alloys in not only H_2S–Cl^- environments but N_2–Cl^- environments such as deaerated seawater [21–31]. Ilevbare and Burstein have proposed that insoluble molybdates can prevent metastable pit from formation and growth [21]. Some researchers have proposed an inhibitor effect of molybdate ions [24–29]. The inhibitor effect of molybdate ions has been also proposed as the role of alloyed molybdenum in H_2S–Cl^- environments [16,32]. However, Ueda and Kudo have proposed the role of alloyed molybdenum in H_2S–Cl^- environments which was different from that in N_2–Cl^- environments [33]. They have proposed that stable molybdenum sulfide can block dissolved H_2S resulting in an enhancement in the formation of protective chromium oxide film. There are many suggestions as to the role of alloyed molybdenum in H_2S–Cl^- environments, but it has not been fully elucidated yet.

The purpose of present work is to elucidate the role of alloyed molybdenum on corrosion resistance of Ni–Cr–Mo–Fe alloys in H_2S–Cl^- environments. Firstly, corrosion resistance of laboratory-melted Ni–Cr–Mo–Fe alloys was investigated to confirm the effect of alloyed molybdenum in the H_2S–Cl^- environment. Secondly, the surface film which formed in the H_2S–Cl^- environment was analyzed. Furthermore, ion selectivity, which is an index of ion permeation, was evaluated using membrane potential measurement

* Corresponding author at: 1-8 Fuso-Cho, Amagasaki, Hyogo 660-0891, Japan. Tel.: +81 6 6489 5716.
E-mail address: tomio.7ae.akiko@jp.nssmc.com (A. Tomio).

Table 1
Chemical compositions of alloys used (mass%) and yield strength (YS) after cold working.

Material	C	Mn	S	Ni	Cr	Mo	Fe	YS (MPa)
A1	0.002	1.00	0.001	60.01	16.02	0.19	Bal.	751
A2	0.002	1.02	0.001	60.01	16.11	4.07	Bal.	794
A3	0.004	1.03	0.001	60.11	15.99	7.98	Bal.	868
A4	0.005	0.96	0.001	60.18	16.10	16.10	Bal.	868
B1	0.003	1.01	0.001	60.13	<0.01	16.03	Bal.	–

to investigate the property of sulfide film formed on the surface. Finally, the role of alloyed molybdenum is discussed based on the obtained results and the stability of sulfide.

2. Experimental Procedure

2.1. Materials

To investigate the effect of alloyed molybdenum on the corrosion resistance in the H_2S–Cl^- environment, four austenitic 60%Ni–16%Cr–x%Mo–Fe alloys containing approximately 60 mass% Ni, 16 mass% Cr, and 0, 4, 8 and 16 mass% Mo were prepared using a vacuum induction melting process. These alloys contained a very low level of sulfur to avoid the effect of sulfide inclusion such as manganese sulfide on localized corrosion resistance [34–42]. Table 1 lists the chemical compositions and the yield strength (YS) of 60%Ni–16%Cr–x%Mo–Fe alloys. These ingots were melted in the laboratory and the plates were obtained by hot rolling, solution heat treatment, followed by final cold work hardening. Considering the difference of workability, the various reductions in thickness during the cold–work process was used to obtain the proper YS. In addition, an austenitic 60%Ni–0%Cr–16%Mo–Fe alloy which did not contain chromium was also prepared using the vacuum induction melting process to investigate the effect of alloyed molybdenum on the corrosion resistance of the Ni–Mo–Fe alloy. Table 1 also lists the chemical compositions of the 60%Ni–0%Cr–16%Mo–Fe alloy. The ingot was melted in the laboratory, the plates were obtained by the hot rolling, and solution heat treatment.

2.2. Stress Corrosion Cracking Test

Slow Strain Rate Test (SSRT) was conducted to evaluate SCC susceptibility of these alloys. This test method conformed to the NACE Standard TM0198-2004 [43]. Uniaxial tensile test specimens were used for this test. The size of test specimens was 3.81 mm OD at the gauge portion and 25.4 mm of the gauge length. The test was conducted in an autoclave at 121 °C. The inert condition comprised deionized water, the gas phase was 0.7 MPa N_2. The hostile condition comprised 25 mass% sodium chloride (NaCl), saturated NaCl solution, with 0.5 mass% acetic acid, the gas phase was 0.7 MPa H_2S. The strain rate in SSRT was 4×10^{-6} s^{-1}. Two replicates were tested in the hostile condition. The test results were evaluated by comparing reduction in cross-sectional area between the inert condition and the hostile condition.

2.3. Electrochemical Measurement

The electrochemical measurement of the 60%Ni–16%Cr–x%Mo–Fe alloy and 60%Ni–0%Cr–16%Mo–Fe alloy was conducted to evaluate the effect of alloyed molybdenum in the corrosion behavior of these alloys. Solution annealed materials were used for the measurement. The size of test specimens was 15 mm in diameter and 2 mm in thickness and the measurement area was approximately 1 cm². These specimens were finished with silicon carbide No. 800 paper, rinsed with deionized water, degreased in

acetone. The 60%Ni–16%Cr–x%Mo–Fe alloys were passivated in 30 mass% nitric acid at 60 °C as a pretreatment. The center of the specimen was abraded with silicon carbide No. 600 paper before the measurement to remove the passivation film which formed in air. The test was conducted in a glass cell at 70 °C. The test solutions comprised 25 mass% NaCl with 0.5 mass% acetic acid and the gas phase was 0.1 MPa H_2S. Polarization curves were obtained potentiodynamically at a sweep rate of 20 mV min^{-1} using a potentiostat after immersion in the test solution for 10 min. A saturated calomel electrode (SCE) was used for a reference electrode and a platinum electrode was used for a counter electrode. A glass filter was used between the reference electrode and the solution to prevent the reference electrode from pollution by H_2S and sulfide. The other two conditions, N_2–Cl^- environment and sulfuric acid-saturated H_2S, were conducted for the measurement of the 60%Ni–0%Cr–16%Mo–Fe alloy to evaluate the influence of H_2S and chloride ions on the corrosion behavior of this alloy. In the N_2–Cl^- environment, the test solution comprised 25 mass% NaCl with 0.5 mass% acetic acid and the gas phase was 0.1 MPa N_2. In the sulfuric acid-saturated H_2S, the test solution comprised 1 mass% sulfuric acid and the gas phase was 0.01 MPa H_2S.

2.4. Surface Analysis

The surface analysis using Augur Electron Spectroscopy (AES) was conducted to evaluate the effect of alloyed molybdenum on a surface condition. The size of the specimen was 15 mm in diameter and 2 mm in thickness and it was finished with buffing, rinsed with deionized water, and then degreased in acetone. The specimens were immersed in the solution which was 0.1 MPa H_2S, 70 °C and 25 mass% NaCl with 0.5% acetic acid for 24 h. AES (PHI 6800) was used to determine the distribution of alloyed elements across the film. The acceleration voltage of AES analysis was 3 kV. The Ar$^+$ ion was used for sputtering and the depth from the surface was estimated from the sputtering depth of SiO_2 as a reference.

2.5. Membrane Potential Measurement

The membrane potential measurement of sulfide was conducted to evaluate the ion selectivity of sulfide. Commercial powders of FeS, Ni_3S_2, and MoS_2 (Kishida Chemical Co. Ltd.,) were used for the measurement. The purity of each reagent was 99.9%, 99.9%, and 99.5%, respectively. The test reagents were mixed with a moderate amount of polytetrafluoroethylene powder, and then they were pressed into a circular disk. Furthermore, commercial anion or cation permeable membranes were also evaluated for comparison. The measurement was conducted according to the method reported by Miyuki et al. [44]. Fig. 1 shows the schematic illustration of the equipment to measure membrane potential. A solution in one cell was 0.01 mol/L potassium chloride (KCl) and a solution in another cell ranged from 1×10^{-3} mol/L to 1 mol/L KCl. The measurement was conducted at room temperature and not under deaerated conditions. One of the sulfide disks was set between the two cells, and then the membrane potential was measured using two saturated Ag/AgCl reference electrodes.