Alloying Effects of Molybdenum and Niobium on Chromium Bearing Low Alloy Steel for Water Ballast Tank

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This study examines the effects of chromium (Cr), molybdenum (Mo) and niobium (Nb) alloying on the corrosion properties of low alloy steel for water ballast tank using electrochemical tests for 15 days in artificial seawater and surface analyses. The EIS and LPR tests revealed the outstanding corrosion resistance Cr+Mo+Nb bearing steel. An SEM analysis after 15 days immersion in the artificial seawater indicated that, among the tested specimens, the Cr+Mo+Nb bearing steel formed the smoothest rust layer with the least cracks. An EPMA analysis for the cross section of the rust layer confirmed that the Nb elements of the Cr, Cr+Nb, and Cr+Mo+Nb bearing steels were enriched at the rust layer; however, the Mo element was enriched only at the rust layer of the Cr+Mo+Nb bearing steel, and not at that of the Cr+Mo bearing steel. This finding is because the small grain size of the Cr+Mo+Nb bearing steel results in the formation of more active sites, where a dissolution and precipitation of the alloying elements occurs. For this reason, the Cr, Mo, and Nb elements are concentrated at the rust layer of the Cr+Mo+Nb bearing steel, thereby improving the corrosion resistance of low alloy steel. [doi:10.2320/matertrans.M2017055]

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1. Introduction

The water ballast tank (WBT) is a space within a vessel that balances the shipment by holding or releasing sea water. When the vessel is not sufficiently loaded with seawater, the vessel can capsize; additionally, the vessel propellers are exposed upon the surface of the water and can collide with the seawater surface, resulting in a propulsion-efficiency decrease and the damage of them. These problems can be solved by the flowing of seawater into the WBT of vessels, thereby lowering the center of gravity and the body of the vessel including the propellers.

The WBT-environment condition is affected by harsh corrosion. Within the tanks, because of the exposure to solar heat, the temperature increases up to 60°C, and this promotes the electrolyte dissolution, resulting in a vigorous mass-transport reaction. Furthermore, the seawater that is used by the ballast water contains an on-average 3.5 mass% of NaCl that causes higher corrosion rates. Consequently, several methods for the increasing of the anti-corrosive properties of materials in seawater such as the cathodic protection and the inorganic coating were studied. The cathodic-protection methods, however, generally do not work efficiently because of the wet/dry condition in the upper part of the ballast water in the WBT. Inorganic coating is also not an ideal protection method because of the existing defects in the coatings. Unfortunately, the corrosion rate greatly increases at the coating defects; therefore, the studies on the rise of the corrosion resistance of materials through various methods such as manufacturing processes and alloying are important.

Among the research studies on the alloying elements, chromium (Cr) and molybdenum (Mo) are known as exceptional elements for the reduction of the corrosion rate. The addition of Cr creates a protective passive layer that inhibits the cathodic reaction; furthermore, the Cr alloying creates a fine-grained rust layer that is mainly composed of Cr-substituted goethite (Cr$_x$Fe$_{1-x}$O(OH)) on the surface of weathering steel retarding oxygen (O) diffusion. The Mo ion (MoO$_4^{2-}$) is adsorbed on the oxide layer and changes the ion-selectivity of the precipitate film from anion-selective to cation-selective in chloride (Cl) containing solutions, thereby preventing the dissolution of steels. Numerous studies concerning the effect of minor alloying elements such as Nb, Ti, V, and W have also been conducted. Especially, niobium (Nb) alloying promotes the formation of a protective Nb-oxide layer on the surface of steel in sulfuric-acid environments, resulting in the decrease of the steel dissolution.

Although a high number of research studies on the single effect of alloying elements have been performed, a dearth of investigations of the synergistic effect of a number of alloying elements represents a limitation. To clarify the alloying effects of Cr, Mo, and Nb alloying in low-alloy steels in terms of the WBT, Fe - 0.5 Cr, Fe - 0.5 Cr - 0.05 Nb, Fe - 0.5 Cr - 0.2 Mo, Fe - 0.5 Cr - 0.2 Nb - 0.05 Nb (mass%) steels are evaluated in the present study using electrochemical impedance spectroscopy (EIS), linear polarization (LPR), scanning electron microscopy (SEM), electron probe micro-analysis (EPMA), and X-ray diffraction (XRD).

2. Experimental Procedures

2.1 Specimens and solution preparation

The materials that were used are low-alloy steels that were manufactured by thermomechanical processing where-in Cr, Mo, or Nb is contained. The chemical compositions of the specimens that were used for the experiments are given in Table 1. For recognition convenience, the four bearing-steel specimens are named Cr, Cr+Mo, Cr+Nb, and Cr+Mo+Nb bearing steels, respectively. The 0.1-cm-thick plates of the low-alloy steels were cut into pieces of 0.8 cm × 0.8 cm. All the specimens were ground to the 600 grit and cleaned with distilled water, ethanol and acetone.
These specimens were immersed in 1000 ml of artificial seawater with pH of 8.2, which was made according to ASTM D1141-98 up to 15 days.\textsuperscript{30} The chemical composition of artificial seawater is listed in Table 2. The pH of solution was controlled by 0.1 M NaOH solution. The solution temperature was maintained at a constant of 60°C to reflect the temperature of a solar-beam exposure.

### 2.2 Electrochemical tests
The corrosion properties were evaluated by electrochemical impedance spectroscopy (EIS) and linear polarization (LPR) tests every 5 day for 15 days. All the electrochemical tests were carried out employing multi-potentiostat/galvanostat model VMP-2. At the first immersion, the open-circuit potential (OCP) was measured before the conduction of the electrochemical tests to stabilize the reactions between the surfaces of the specimen and the artificial seawater. All of the electrochemical tests were performed with a conventional three-electrode cell consisting of a specimen as the working electrode, two pure-graphite rods as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode with the use of a Luggin capillary. To prevent leaking of the potassium chloride (KCl) solution in SCE, the end of SCE was sealed with vycor-frit-mounted Teflon tube, and a distilled-water immersion was performed to check the leakage. The low-alloy steel specimens were mounted for efficient surface exposure. To prevent leaking the seawater into the crevice between specimen and mount, the crevice was sealed with black paint and silicon (Si) paste. The EIS measurement was performed using a potentiostat under the OCP with sinusoidal amplitude of 20 mV in the frequency range from 10 kHz to 100 mHz. With the use of the Zsimpwin software, the impedance plots were interpreted on the basis of an equivalent circuit according to a suitable fitting procedure. The LPR tests were conducted at a potential sweep of 0.166 mV/s from an initial potential of −20 mV vs. OCP to a final potential of 20 mV vs. OCP.

### 2.3 Surface analyses
Various surface analyses were carried out to investigate the influence of Cr, Mo and Nb additions on the low-alloy steels for the WBT. The corrosion products that formed on the surface of the specimens were analyzed using the S-3000H scanning electron microscope and the JXA-8900R EPMA device to show the element distribution of the cross-section. The chemical composition of the rust layer was identified using the ESCALAB250 HP-powder XRD device.

### 3. Results and Discussion

#### 3.1 Corrosion rate calculation
The corrosion rates of specimens were calculated from EIS and LPR measurements. By fitting EIS data, the polarization resistance ($R_p$) that is the sum of rust resistance ($R_{rust}$) and charge transfer resistance ($R_{ct}$) can be obtained and then transferred to corrosion current density ($i_{corr}$) and corrosion rate with the use of eqs. (1) and (2), as follows:\textsuperscript{31}

\[
R_p = \frac{\beta_a \beta_c}{2.3 i_{corr} (\beta_a + \beta_c)}
\]  \hspace{1cm} (1)

\[
Corrosion rate (mm/y) = \frac{3.16 \times 10^2 \times i_{corr} \times M}{z F \rho}
\]  \hspace{1cm} (2)

where $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes, respectively, $i_{corr}$ is the corrosion current density ($\mu A/cm^2$), $M$ is the molar mass of the metal (g/mol), $z$ is the number of electrons transferred per metal atom, $F$ is Faraday's constant, and $\rho$ is the density of the metal (g/cm$^3$). The impedance parameters of each specimen including $R_p$ are listed in Table 3. Also, through the linear polarization, the $R_p$ was obtained using the slope of the E-i plot, and this was followed by its transferal to $i_{corr}$ and corrosion rate through the applications of eqs. (1) and (2). The corrosion rates of specimens are shown in Fig. 1. The corrosion rates that were measured using both EIS and LPR decreased in the sequence of the Cr, Cr+Mo, Cr+Nb, and Cr+Mo+Nb bearing steels. The EIS measurement corrosion rate is higher than that of the LPR measurement because the $R_p$ from EIS measurement is compensated for by the solution resistance.

#### 3.2 Electrochemical impedance spectroscopy
The EIS Bode plots for the measurements of the four specimens every five days for 15 days are shown in Fig. 2. The Bode plot shows the impedance parameter ($Z$) and the phase angle as a function of the frequency.\textsuperscript{24} In the Bode plot, the high-frequency $Z$ indicates the solution resistance ($R_s$), while the low-frequency $Z$ indicates the total resistance including the solution and polarization resistances ($R_p$). Figure 3 shows the equivalent electrical circuits for EIS fitting. The circuit of the single time constant that is shown in Fig. 3(a) is applied to the 1st day immersion data of each specimen; while the two-time constant circuit in Fig. 3(b) is applied to 5th day and the three-time constant circuit in Fig. 3(c) is applied to 10th and 15th days immersion data of each specimen in accordance with the formation of the rust layer. At the 5th day, since the effect of alloying elements is insignificant, the circuit as shown in Fig. 3(b) is constructed. However, at the 10th and 15th days, since it is believed that
the effect of the alloying elements appears, the rust layer is separated as shown in Fig. 3(c). In Fig. 3(c), the \( R_{\text{pore}} \) means a region with a small amount of alloying element and the \( R_{\text{dense}} \) means a large amount of it. The capacitance was substituted by CPE (constant phase element) to consider the depression angle and the homogeneity in the system. The impedance of CPE can be described by the following equation.31)

\[
Z_{\text{CPE}} = \frac{1}{Y_0} (j\omega)^n
\]  

where \( Y_0 \) is the magnitude of the CPE (with units \( \Omega^{-1}\text{cm}^{-2}\text{s}^{-n} \)), \( \omega \) is the sine wave modulation angular frequency (rad s\(^{-1}\)), \( n \) defines the imaginary number, and \( n \) is the depression parameter (0 \( \leq n \leq 1 \)). By fitting EIS data, the accurate values of the impedance parameters of each specimen including \( R_s \), \( R_p \), constant phase elements (CPE1, CPE2, CPE3), and depression values are given in Table 3. The results indicate the largest \( R_p \) value of the Cr+Mo+Nb bearing steel, and this means that the rust layer that was formed on the Cr+Mo+Nb bearing steel is the most protective. Also the values of \( R_{\text{dense}} \) are smaller than those of \( R_{\text{ct}} \). Since the \( R_{\text{ct}} \) means the difficulty of the electron movement, it is considered that the alloying element also acts as a separator of lithium ion battery which prevents the movement of electrons but allows the movement of ions.32)

From the Bode plot of EIS, the information of surface/electrolyte solution interface can be explained with the splitting in the phase angle-frequency curve.25) In Fig. 2, all specimens showed a similar trend on the first day that the phase maximum was located between 10\(^1\) and 10\(^2\) Hz of frequency with the angle of approximately 70°. This similarity is because at the initial solution-immersion time, corrosion products were not formed or were only formed weakly. After some immersion time, it seemed clear that the phase maximum of all the specimens shifted toward lower frequencies with immersion time.33–36) The solution-resistance increase was caused by the reactions of conductive ions such as those of chloride (Cl), sulphate (S), and fluoride (F) in the solution with corrosion product forming metals. According to the compositions and properties of corrosion products, the degrees of the phase angle shift and phase angle maxima are different for each specimen. The phase angle of each specimen as a function of frequency after the 15 days of immersion is shown in Fig. 4. The high frequency spectra detected local surface defects, while the low frequency spectra detected processes within the film and at the metal/film interface, respectively.37) In the frequency range between 10\(^{-1}\) and 10\(^1\) Hz, the Cr+Mo+Nb bearing steel has a maximum phase angle nearest from –90° and it has the largest phase angle value compared to the other specimens. This result reveals that the rust layer formed on the surface of Cr+Mo+Nb bearing steel exhibited more pure capacitive behaviour than steel.
other specimens that indicates an improvement of the structural properties of the corrosion products. This is because the Cr+Mo+Nb bearing steel produced a more dense rust layer. The formation of other products could be detected using the phase-angle behaviour of the Bode plot. In Fig. 4, a small slope appeared between the $10^1$ Hz and $10^3$ Hz frequencies in the Bode plots of the Cr+Mo, Cr+Nb, and Cr+Mo+Nb bearing steels, while the only Cr bearing steel showed either nothing or a small slope.

Figure 5 shows the depression angle of dense rust layer of each specimen after 15 days immersion in artificial seawater.
An increase of the depression angle represents the heterogeneity increase of the surface, indicating as increased surface roughness and the formation of porous layers.\textsuperscript{38–42} The depression angle of the only Cr bearing steel is the highest after the 15 days immersion in artificial seawater, while the Cr+Mo+Nb bearing steel showed the minimum depression angle value. This result indicates the roughness of the only Cr bearing steel is higher and its rust layer is more porous than those of the other specimens, while the Cr+Mo+Nb bearing steel represents the most-homogeneous rust layer.

### 3.3 Surface analyses

The SEM and EDS images of the top view for Cr, Cr+Mo, Cr+Nb, and Cr+Mo+Nb bearing steels after the 15 days immersion in the artificial seawater are shown in Fig. 6. Before observation, the spraying of ethanol and the blowing of nitrogen (N\textsubscript{2}) gas removed red-colored iron oxide corrosion products. Then, the black-colored corrosion product that was located under the red-colored corrosion products was observed using the SEM with the EDS. The EDS results indicated that the black-colored corrosion product is composed mainly of Cr and O. The specimen containing only Cr showed the most and largest surface cracks, while the number and the size of the cracks on the surface of the Cr+Mo
and Cr+Nb bearing steels decreased. Lastly, Cr+Mo+Nb bearing steel showed the smoothest surface without any cracks. The addition of the Cr is beneficial for the formation of a protective Cr-rich layer on the surface of the steel. An aggressive ion such as Cl ion could enter through the cracks formed on the surface and then react with the steel. Therefore, it is expected that the Cr+Mo+Nb bearing steel comprises the most durable rust layer that prevents the penetration of aggressive ions.

The EPMA analysis for the cross-section of the specimens was conducted to determine the distribution of the alloying elements along the depth. Figure 7 shows that all of the specimens formed rust layers that are composed of Fe, O, and Cr on the surface. Due to the small Mo and Nb contents, their distribution could not be shown with EPMA mapping; therefore, the Mo and Nb distribution were detected using the EPMA line profile. Figure 8 shows the EPMA line profile of the Cr, Mo, and Nb for all of the specimens. All of the specimens showed higher Cr intensities at the rust layer formed on the surface of specimens. The Nb intensities of the Cr+Nb and Cr+Mo+Nb steels increased at the rust layer; however, the Mo intensities of the Cr+Mo and Cr+Mo+Nb bearing steels showed different trends. In the Cr+Mo bearing steel, the Mo intensity remained constant through rust layer and substrate, while the Cr+Mo+Nb bearing steel showed a higher Mo intensity at the rust layer. This could be explained by microstructures. The optical microstructure images of each specimen are shown in Fig. 9. The grain size of the Cr+Mo+Nb bearing steel is smaller than that of the Cr+Mo bearing steel, resulting in a larger grain boundary area with a higher active energy compared to grain. The anodic dissolution reaction occurred more frequently at the grain boundaries so that greater quantities of the alloying elements can be dissolved from the parent steel. Then, the dissolved elements that precipitated at the surface of the substrate formed corrosion products. The Cr+Mo+Nb bearing steel with the higher amount of alloying elements formed a greater quantity of corrosion products including the Cr, Mo, and Nb, this results in high Cr, Mo, and Nb enrichments on the surface of the substrate after some immersion times; this result can be confirmed by the Rp value in Table 3. The Rp of the Cr+Mo+Nb bearing steel is less than that of the Cr+Mo bearing steel on the first immersion day when the rust layer had not formed. The Rp value of the Cr+Mo+Nb bearing steel, however, increased with the immersion time and is larger than that of Cr+Mo bearing steel after 5 days immersion. Both the Mo and Nb additions were proved as effective in the lowering of the transformation temperatures, and a greater effectiveness was observed regarding the Mo and the Nb in the ferritic and bainitic regions, respectively. Especially, the Nb is particularly effective in the retardation of the recrystallization, thereby efficient for grain refinement. Mo is also known as an alloying element for the retardation of the ferrite formation, and this is efficient for lowering bainitic transformation temperature, and especially in terms of its assistance of the Nb for the recrystallization retardation. Because of these effects, the rust layer that is enriched by Cr, Mo, and Nb was formed on the Cr+Mo+Nb bearing steel that comprises finer grains and a more active site.

The corrosion products that formed on the surface of specimens were analyzed using XRD. The XRD patterns of the specimens that were immersed in artificial seawater for 15 days are shown in Fig. 10. As can be seen in EPMA mapping images, all of the specimens formed a Cr-rich layer that is adherent to the surface; therefore, a common feature that
is evident in all of the X-ray diffractograms is the predominance of the Fe and Cr at a 2theta angle of nearly 44 degrees and the prevalence of Cr$_2$O$_3$ and FeCr$_2$O$_4$. Additionally, in the X-ray diffractograms for the only Cr bearing steel, the Fe$_2$O$_3$ peaks are present. Also, the Cr+Mo bearing steel showed the XRD peak of the Fe$_2$MoO$_4$ and the Cr+Nb bearing steel showed NbO. Lastly, the Cr+Mo+Nb bearing steel
showed the Fe₂MoO₄ and NbO peaks. The comparison of these results with the depression-angle trend indicates that the formation of the Fe₂MoO₄ and NbO compounds reduced the porosity and the roughness of the Cr+Mo+Nb bearing steel, while the Fe oxide could not form the protective rust layer.

4. Conclusions

The EIS and LPR measurements confirmed that the addition of the 0.5 mass% Cr, 0.2 mass% Mo, and 0.05 mass% Nb to the low-alloy steel for the WBT is the most effective for improvement of the corrosion resistance. The EIS measurement showed that the Cr+Mo+Nb bearing steel formed the most homogeneous rust layer of which degradation is the least for the 15 days artificial seawater immersion. The EPMA results indicated that the Cr and Nb elements are concentrated at the rust layers of the Nb-containing specimens; however, while the Mo element is enriched at the rust layer of the Cr+ Mo+Nb bearing steel, it is not concentrated at the rust layer of the Cr+Mo bearing steel. This phenomenon occurred due to the finer grain size of the Cr+Mo+Nb bearing steel that comprises more grain boundaries and leads to the dissolution and precipitation of higher quantities of the alloying elements in the Cr₂O₃, FeCr₂O₄, Fe₂MoO₄, and NbO forms. Therefore, the rust layer that is enriched by Cr, Mo, and Nb improved the corrosion resistance of Cr+Mo+Nb bearing steel.

REFERENCES