Alloying Effect of Chromium on the Corrosion Behavior of Low-Alloy Steels

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Alloying effect of Cr in the interaction with other elements in low alloy steel for corrosion resistance was designed and prepared. The corrosion behavior of the alloy immersed in mild acid–chloride solution (200 atomic ppm Cl− and pH 4) at room temperature in an ambient condition has been studied by electrochemical laboratory tests (potentiodynamic polarization test, potentiostatic test, electrochemical impedance spectroscopy) and surface analyses (SEM, XPS). The results reveal that Cr addition improved the localized corrosion resistance by promoting the formation of beneficial Fe and Cu compounds on the protective films of 0.1 and 0.3 mass% Cr steels. However, the over-alloying circumstance in 0.5 mass% Cr steel caused the negative effect of Cr addition due to metal chloride-induced hydrolysis which accelerated the propagation of the localized corrosion. To summarize, 0.3 mass% Cr addition was determined to be the optimum value for alloying to blank steel.

Keywords: chromium, acid rain, electrochemical impedance spectroscopy, X-ray photoelectron spectroscopy


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1. Introduction

Acid deposition is the scientific term used to describe “acid rain”, which is a widespread term used to describe all forms of acid deposition: wet deposition (rain, snow, sleet and hail (also called acid precipitation)), dry deposition (gases, particles and vapor) and cloud or fog deposition. Acid precipitation is typically acidic, due to the reaction of water with naturally occurring carbon dioxide in the atmosphere. Atmospheric pollutants such as oxides of sulfur and nitrogen increase the acidity of the precipitation as they are converted to sulfuric and nitric acids. Rainfall from un-polluted air usually has a pH of 5.6 and rainfall with pH < 5.6 is considered acid rain. The average pH of precipitation is about 4.6–4.7. This low pH value obviously negatively affects soils, water quality, forest, animals and human health. Moreover, structural damage to underground pipes, cables and foundations submerged in acid water can also occur, in addition to damage to exposed buildings, bridges and vehicles.

This study focuses on the corrosion of steels in acid rain environment. While dry deposition contributes to steel corrosion, in most areas with substantial rainfall the effect of wet deposition on the steel surface is more damaging. The interactions between the material surface and acid deposition vary depending on the amount of exposure, the reactivity of the different materials and the humidity.

In order to prevent the acid deposition-induced deterioration of steels, zinc alloy coatings, acid-resistant paints and lubricating oil coatings, etc. have been applied. However, modification to the steel composition by the use of alloying elements is the most attractive method due to the reduced manufacture expenses and maintenance costs that can be achieved. Low alloy steels with excellent mechanical properties and relatively low price derive their enhanced corrosion resistance from the inclusion of up to 2 mass% of such key alloying elements as copper, phosphorus, chromium, nickel and silicon, etc. This steel is called weathering steel. The weathering steel forms the protective rust (corrosion product) layer, which is dense and adherent to steel, during a long-term exposure to the atmosphere. Therefore, this protective rust layer reduces corrosion rate of steel. The corrosion resistance of weathering steel was improved about twice compared to that of carbon steel. In particular, Cr compounds in the rust layer of Cr-containing weathering steels partly replace iron species in the corrosion products to produce a more protective rust layer. Chromium in low carbon steels forms protective Cr compounds in the inner region of the rust layer in synthetic potable water. The enrichment of Cr in the rust layer acts as a barrier to corrosion.

The objective of this research is to study the alloying effect of Cr in low alloy steel for corrosion resistance. Electrochemical laboratory tests such as potentiodynamic polarization test, potentiostatic test (accelerated test) and alternating current (AC) impedance measurement provide useful data about the corrosion behavior. In addition, surface analyses after testing (scanning electron microscopy, SEM, X-ray photoelectron spectroscopy, XPS) were conducted to examine the protective mechanisms of rust layers. These results will contribute to the development of a new weathering steel system and facilitate the prediction of the limits for alloying element addition for subsequent research.

2. Experimental Procedures

2.1 Materials

The alloying process of low-alloy steels in this study consisted of two stages: hot and cold working. In the former, the mixture of the constituent elements was heated to 1523 K, held for 1 h, then subjected to hot rolling to reduce the steel thickness from 20 to 3.4 mm, and finally annealed in a temperature range of 1143–1253 K. For ease of storage and moving, the semifinished steel was rolled in a cooling temperature of 873 K for 1 h, and then cooled in a furnace. In the subsequent cold working stage, the semifinished steel was cleaned in HCl, cold rolled at room temperature in order to reduce the steel thickness from 3.2 to 1.2 mm, and finally annealed at 1103 K for 30 s for steel refinement.

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The 1.2 mm-thick plates of low alloy steels were cut into pieces of 15 mm × 15 mm. The chemical compositions of these steels is given in Table 1. Only the Cr content differed among the steels.

### 2.2 Electrolyte

A mild acid–chloride solution was used to simulate an acid rain environment in the atmospheric corrosion condition. A chloride containing environment is very corrosive. All measurements were carried out in 1000 mL of acid–chloride solution, that was mixed with the same volume of aqueous solution of $6.25 \times 10^{-5}$ mol L$^{-1}$ H$_2$SO$_4$ and $5.5 \times 10^{-3}$ mol L$^{-1}$ NaCl (which yields 200 atomic ppm Cl$^-$ and pH 4) at room temperature in ambient condition.

### 2.3 Electrochemical measurements

Each specimen was cast in a mould using hot acrylic powder, ground by 800-grit silicon carbide (SiC) paper, degreased in an ultrasonic cleaner with ethanol for 300 s, cleaned with distilled water and dried in hot air. To prevent the initiation of crevice corrosion between the mould and specimen, the mould/specimen interface was sealed with silicon sealant, leaving an exposed area of 100 mm$^2$ on the material surface.

The electrochemical measurements consisting of potentiodynamic polarization tests, potentiostatic tests, electrochemical impedance spectroscopy (EIS) measurements were conducted in a three-electrode electrochemical system. Figure 1 shows schematic of three-electrode electrochemical system. A saturated calomel electrode (SCE) and two pure graphite rods were used as the reference and counter electrodes, respectively. The specimen was allowed to attain a stable open circuit potential (OCP) before each electrochemical measurement. A period of about 4.5 ks was required for the OCP to become stable within ±5 mV.

Potentiodynamic polarization tests were performed to evaluate the overall corrosion behavior of the specimens using a potentiostat (EG&G Instruments Model 263A) connected to a computer system. The potential of the electrode was swept at a rate of 0.167 mV s$^{-1}$ from the initial potential of $-250$ mV$_{OCP}$ to the final potential of $+1000$ mV$_{SCE}$. The potentiostatic tests were conducted at an applied potential of 0 mV$_{SCE}$ to examine the tendency of pit propagation as a function of Cr content for 10 h using a multi-Potentiostat (Bio-Logic, Model VPM2). In order to get a better understanding of the effect of Cr on the corrosion behavior of low alloy steel in a short immersion time, EIS measurements were carried out using a potentiostat/galvanostat/FRA [Frequency Response Analyser] (EG&G, Model Parstat 2263). The first EIS measurement was obtained at OCP with an amplitude of 20 mV in the frequency range from 100 kHz to 10 mHz, then this process was daily repeated for 7 days. To insure reproducibility, at least three repetitions were run for specimen.

### 2.4 Surface analysis

To investigate the relationship between the alloying element components and the surface morphology of the corrosion products, the surface was examined using XPS after 7-day immersion. The corroded surface features after 7-day immersion, and the surface images after potentiostatic tests were inspected by SEM.

### 3. Results and Discussion

#### 3.1 Potentiodynamic polarization test

Figure 2 shows the potentiodynamic polarization curves of specimens in acid–chloride solution (200 ppm Cl$^-$, pH 4). In general, all steels demonstrated active corrosion behavior and no passivation, indicating that the anodic current density continuously increased with increasing potential. This behavior normally means that a passive film is not formed on the surface of the material.

The potentiodynamic polarization tests indicated that Cr addition slightly changed the corrosion potential of the blank steel and the anodic current density. The anodic current density initially decreased as Cr content was increased from 0.1 to 0.3 mass% Cr, but then increased as Cr content was raised further to 0.5 mass% Cr.

### Table 1 Chemical compositions of specimens (mass%).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Co</th>
<th>S</th>
<th>Cu</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank steel</td>
<td>0.07</td>
<td>0.25</td>
<td>0.7</td>
<td>0.05</td>
<td>0.01</td>
<td>0.35</td>
<td>—</td>
<td>balance</td>
</tr>
<tr>
<td>0.1Cr steel</td>
<td>0.07</td>
<td>0.25</td>
<td>0.7</td>
<td>0.05</td>
<td>0.01</td>
<td>0.35</td>
<td>0.1 balance</td>
<td></td>
</tr>
<tr>
<td>0.3Cr steel</td>
<td>0.07</td>
<td>0.25</td>
<td>0.7</td>
<td>0.05</td>
<td>0.01</td>
<td>0.35</td>
<td>0.3 balance</td>
<td></td>
</tr>
<tr>
<td>0.5Cr steel</td>
<td>0.07</td>
<td>0.25</td>
<td>0.7</td>
<td>0.05</td>
<td>0.01</td>
<td>0.35</td>
<td>0.5 balance</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2 Potentiodynamic polarization curves of specimens in acid–chloride solution (200 ppm Cl⁻, pH 4).

3.2 Potentiostatic test

The results of the potentiostatic test performed at an applied potential of 0 mV\text{SCE} are shown in Fig. 3. The current density initially increased and then remained almost constant throughout the experiment, indicating that sufficient Cr addition increased the corrosion resistance. The current density of the steels in the steady state decreased with increasing Cr content, except that of 0.5 mass% Cr steel, in the following order: 0.3 mass% Cr steel (28 µA mm⁻²) < 0.1 mass% Cr steel (32 µA mm⁻²) < blank steel (37 µA mm⁻²) < 0.5 mass% Cr steel (45 µA mm⁻²). This indicated that the addition of 0.1 or 0.3 mass% Cr slowed down the corrosion rate of steels, whereas the addition of 0.5 mass% Cr accelerated the corrosion process of blank steel. These potentiostatic results were totally consistent with potentiodynamic results.

3.3 Electrochemical impedance spectroscopy (EIS) measurements

Nyquist plots for the specimens in acid–chloride solution (200 ppm Cl⁻, pH 4) at various immersion intervals under OCP are presented in Fig. 4. The impedance spectra of the steels showed a very small semicircle in the higher frequency region and a large semicircle in the lower frequency region, indicating the formation of a rust layer on the steel surface. This two-time constant behavior was caused by the reaction between the specimen and electrolyte and simultaneously between the rust layer and electrolyte. Based on the above impedance spectrum features, the physical model and equivalent circuit for fitting the EIS data are presented in Fig. 5. The circuit consists of the following elements: a solution resistance, $R_s$, two constant phase element, CPE1 and CPE2, CPE1, the dielectric constant of the rust and water absorbed by the film, CPE2, the capacitance generated by the metal dissolution reaction and by the electric double layer at the water/substrate interface, a rust layer resistance, $R_{rust}$ and a charge transfer resistance, $R_{ct}$. CPE is used instead of a capacitor to compensate for the non-homogeneity in the system frequency, where the CPE contains a double-layer capacitance, C and phenomenological coefficient, n.

The fitted EIS data obtained by ZSimpWin (EChem Soft, ver 3.0) program are presented in Table 2. The $R_{ct}$ values were much higher than $R_{rust}$ values in all cases, indicating the formation of a very thin rust layer on the steel surface and that the steel corrosion procedure was completely controlled by $R_{ct}$. The total polarization resistance, $R_p$ was equal to the sum of the $R_{rust}$ and $R_{ct}$ values. Moreover, the diameter of the large arc in the Nyquist plots can be regarded as $R_p$. A decrease in the diameter of the arc reflected a decrease in $R_p$ and vice versa.

The corrosion current density of the steels was calculated by the following equation, under the assumption that $\beta_a$ and $\beta_c$ were equal 0.1 V decade⁻¹:27)

$$i_{corr} = \frac{\beta_a \beta_c}{2.3 \nu_R (\beta_a + \beta_c)}$$

where $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes, respectively and $i_{corr}$ is the corrosion current density of each specimen.

The corrosion rate, $k$ can be inferred from the corrosion current density, $i_{corr}$, based on Faraday’s law:28)

$$corrosion\ rate, \ k \ (mm \cdot y^{-1}) = \frac{0.00327i_{corr}W_E}{\rho}$$

where 0.00327 is the metric and time conversion factor, $i_{corr}$ (µA cm⁻²) the corrosion current density, $W_E$ (g) the equivalent weight of specimen and $\rho$ (g cm⁻³) the density of specimen.

Figure 6 exhibits the progression of the corrosion rates as a function of time in the EIS measurements. As shown in Table 2, Figs. 4 and 6, the corrosion rate relatively increased with time but decreased with increasing Cr content, except for the 0.5 mass% Cr steel. At the early stage of the immersion period, the corrosion rate of the 0.5 mass% Cr steel was lower than that of the blank steel. This state was maintained up to the fourth day. While the corrosion rate of
A blank steel immediately decreased and then increased, that of 0.5 mass% Cr steel continuously increased. At the later stage of the immersion period, the corrosion rate of the 0.5 mass% Cr steel was higher than that of the blank steel, confirming the beneficial effect of the 0.5 mass% Cr addition at the early stage of immersion. After sufficient time, the rust layer structure underwent a change due to the negative effect of the alloying element, leading to a decrease in the corrosion resistance. The EIS measurements for the average corrosion rates exhibited complete agreement, as shown in Fig. 7, the steel corrosion rates were ranked in the following order: 0.3 mass% Cr steel (0.126 mm·y⁻¹) < 0.1 mass% Cr steel (0.132 mm·y⁻¹) < blank steel (0.151 mm·y⁻¹) < 0.5 mass%
Cr steel (0.161 mm·y⁻¹). Moreover, they were consistent with the results of the potentiodynamic polarization and potentiostatic tests.

The Nyquist plot (Fig. 4) shows depressed semi-circles centred below the real axis. The depression angle, \( \alpha \) from the real axis in a Nyquist representation is an omnipresent characteristic of EIS measurements. The depression angle of the semicircles was determined from the position of the centre of the semicircles on the complex plane diagrams. The depression angle, \( \alpha \), in their mathematical fitting procedures as an empirical factor that would appear as an exponent \( (\alpha) \), with values between 0 and 1 added to the imaginary term of an RC circuit; the model thus assumes that the deviation from ideality is caused purely by the capacitive behaviour of the interface.\(^3\) The calculated depression angle was obtained from the three-electrode probe data shown in Table 2. The depression angle, \( \alpha \) (degree) is calculated by the following equation:\(^{34}\)

\[
\alpha = 2(1 - n)/\pi \tag{3}
\]

The increase of the depression angle expresses the increase of the surface roughness.\(^{25,36}\) The surface roughness of the 0.5 mass% Cr steel was higher than that of the blank steel with increasing time because an increasing depression angle
is observed and an increasingly marked localized corrosion takes place on the surface.

Finally, all experimental data supported the finding that the corrosion behavior of low-alloy steel was improved by the addition of up to 0.3 mass% Cr. The addition of 0.1 and 0.3 mass% Cr improved the corrosion rate of the blank steel by about 10 and 20%, respectively. However, the addition of 0.5 mass% Cr accelerated the corrosion process of the steel. This important characteristic was attributed to the negative effect of an excessive amount of Cr on the formation of a protective film on the steel surface. When the Cr content exceeded the critical point of 0.5 mass% Cr, the overall effect of the alloying element became negative, thereby decreasing the corrosion resistance.

3.4 Surface analysis

The electrochemical measurements only supported the final conclusion regarding the effectiveness of the Cr addition on the steels’ corrosion resistance. However, to determine the mechanism of this effect on the corrosion behavior of the blank steel after Cr addition, surface analyses were also conducted.

According to the SEM images presented in Fig. 8 of the surface morphology after 7-day immersion, all steel surfaces were deformed under the localized corrosion with different intensities. The corrosion in the blank steel started as cracks which developed into pits. Pitting corrosion occurred on the 0.1 and 0.3 mass% Cr steel surfaces, but the pit size and density of the 0.1 mass% Cr steel was larger than that of the 0.3 mass% Cr steel. However, the pitting corrosion exhibited the highest density on the 0.5 mass% Cr steel surface. To summarize, the trend and cause of the corrosion behavior of all steels after 7-day immersion were similar to those revealed in the potentiostatic test.

The SEM observation of the corroded surfaces after the potentiostatic tests is displayed in Fig. 9. These images show the non-uniform corrosion on the steel surfaces. The outer layer on the blank steel surface was deeply removed. Localized corrosion occurred on the 0.1 mass% Cr steel surface at higher density than on the 0.3 mass% Cr steel surface, indicating the improved corrosion resistance of the low alloy steel gained by increasing the Cr content. However, the highest density of pits appeared on the 0.5 mass% Cr steel surface confirming that it was heavily corroded. This increased corrosion was assumed to have resulted from over-alloying circumstance which accelerated the corrosion process.

To further elucidate the surface characteristics of the tested steels, their surface products after 7-day immersion were examined by XPS analysis (Fig. 10(a)). The XPS spectra revealed Fe, Cu and Cr peaks, as these elements were the most effective factors in the formation of the protective film on the steel surfaces. The steel surface products obtained from the analysis of the XPS peaks are listed in Table 3.47-49 Chemical compounds, such as Fe₂O₃, FeOOH, CuO and Cu(OH)₂, were detected on the surface of specimens shown in XPS spectra. Surprisingly, there was no Cr peak in the binding energy range of 573–585 eV where the Cr peaks predominated, indicating that no Cr oxides formed on the outer layer of the protective films. However, the beneficial Cr compounds might concentrate behind the protective film since Cr compounds often tend to form in the inner region of rust layers.45-48 The formation of Cr compounds on the inner region of rust layers inhibits anodic dissolution of the iron component and promotes the formation of ferrous oxides, thereby reducing the corrosion rate. Although Cr peaks were not detected in the outer layer, it is possible to infer the Cr oxide formation on the inner region of rust layers, confirming that the increasing amounts of ferrous oxides formation on the outer layer of the protective films.49

In Fig. 10(b), the Cu peak did not appear in the XPS spectra of the blank steel but did in that of the Cr-alloyed
steels, indicating that the Cr addition activated the effect of Cu in low alloy steel under the acid-chloride environment. The Cu peak was the highest in the 0.3 mass% Cr steel and the lowest in the 0.5 mass% Cr steel. Cu oxides on the surface of the specimens improve the corrosion resistance of the Cu-containing steel.\textsuperscript{50} Cupric hydroxide Cu(OH)\textsubscript{2} has been reported to be less stable than cupric oxide CuO.\textsuperscript{51}

Figure 10(c) shows that the addition of 0.5 mass% Cr considerably reduced the intensity of the Fe peak, indicating that over-alloying circumstance dramatically dissolved the beneficial Fe compounds on the protective film of 0.5 mass% Cr steel, thereby increasing the corrosion rate of the 0.5 mass% Cr steel compared to that of the other steels.

Clearly, Cr addition affected the corrosion behavior of the low alloy steels. The absence of the beneficial Cr compounds on the outer layer of the protective film was due to the presence of chloride in the solution. Chloride is well-known for its ability to penetrate and destroy protective films on steel. Chromium hydroxide (Cr(OH)\textsubscript{3}) and chromium oxide (Cr\textsubscript{2}O\textsubscript{3}) are the only known compounds capable of retaining a protective coating in a free-chloride solution.\textsuperscript{20} In the case

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Fig. 9  SEM images of corroded surface of specimens after potentiostatic tests: (a) blank steel, (b) 0.1 mass% Cr steel, (c) 0.3 mass% Cr steel and (d) 0.5 mass% Cr steel.

Fig. 10 XPS spectra of alloying elements from the corroded surface of specimens after 7-day immersion in acid-chloride solution (200 ppm Cl\textsuperscript{-}, pH 4): (a) survey spectra, (b) Cu and (c) Fe.
Table 3 XPS peak analysis for surface products of steels.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Peak</th>
<th>Energy (eV)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank steel</td>
<td>Fe2p1/2</td>
<td>711.0(^{37})</td>
<td>FeO(_2)</td>
</tr>
<tr>
<td>Blank steel</td>
<td>Fe2p3/2</td>
<td>724.3(^{39})</td>
<td>FeOOH</td>
</tr>
<tr>
<td>0.1Cr steel</td>
<td>Fe2p1/2</td>
<td>711.0(^{37})</td>
<td>FeO(_2)</td>
</tr>
<tr>
<td>0.1Cr steel</td>
<td>Fe2p3/2</td>
<td>724.3(^{39})</td>
<td>FeOOH</td>
</tr>
<tr>
<td>0.1Cr steel</td>
<td>Cu2p1/2</td>
<td>934.7(^{38})</td>
<td>Cu(OH)(_2)</td>
</tr>
<tr>
<td>0.1Cr steel</td>
<td>Cu2p3/2, sat</td>
<td>943.0(^{35})</td>
<td>CuO</td>
</tr>
<tr>
<td>0.1Cr steel</td>
<td>Cu2p3/2</td>
<td>953.7(^{36})</td>
<td>CuO</td>
</tr>
<tr>
<td>0.3Cr steel</td>
<td>Fe2p1/2</td>
<td>711.1(^{38})</td>
<td>FeO(_2)</td>
</tr>
<tr>
<td>0.3Cr steel</td>
<td>Fe2p3/2</td>
<td>724.3(^{39})</td>
<td>FeOOH</td>
</tr>
<tr>
<td>0.3Cr steel</td>
<td>Cu2p1/2</td>
<td>934.4(^{42})</td>
<td>Cu(OH)(_2)</td>
</tr>
<tr>
<td>0.3Cr steel</td>
<td>Cu2p3/2, sat</td>
<td>943.0(^{35})</td>
<td>CuO</td>
</tr>
<tr>
<td>0.3Cr steel</td>
<td>Cu2p3/2</td>
<td>953.7(^{36})</td>
<td>CuO</td>
</tr>
<tr>
<td>0.5Cr steel</td>
<td>Fe2p1/2</td>
<td>711.1(^{38})</td>
<td>FeO(_2)</td>
</tr>
<tr>
<td>0.5Cr steel</td>
<td>Fe2p3/2, sat</td>
<td>718.6(^{40})</td>
<td>O(_2)/Fe/Cu</td>
</tr>
<tr>
<td>0.5Cr steel</td>
<td>Fe2p3/2</td>
<td>724.3(^{39})</td>
<td>FeOOH</td>
</tr>
<tr>
<td>0.5Cr steel</td>
<td>Cu2p1/2</td>
<td>934.4(^{42})</td>
<td>Cu(OH)(_2)</td>
</tr>
<tr>
<td>0.5Cr steel</td>
<td>Cu2p3/2</td>
<td>943.0(^{35})</td>
<td>CuO</td>
</tr>
<tr>
<td>0.5Cr steel</td>
<td>Cu2p3/2</td>
<td>953.7(^{36})</td>
<td>CuO</td>
</tr>
</tbody>
</table>

of the 0.1 and 0.3 mass% Cr steels, the Cr concentration was sufficient to act as a barrier to steel dissolution, which enhanced the steels’ corrosion behavior through the formation of Cr oxides on the inner layer of the protective films.\(^{45-49}\)

However, the higher Cr content in the 0.5 mass% Cr steel induced the negative effect of alloying. Al-Hajji et al. also reported the same negative effect of Cr addition to steels in a sour brine solution (pH 4.25).\(^{51}\) In addition, other studies indicated that Cr addition to steels increased the rates of dissolution in hydrochloric acid and other acidic environments.\(^{52,53}\) The over-alloying circumstance of Cr leads to steel deterioration in acid–chloride solution due to the hydrolysis of metal chlorides. In the initiation of localized steel corrosion, the pH in the concentration cell was mainly controlled by the hydrolysis of Fe\(^{2+}\) at pH values higher than 3.8. According to the potential-pH equilibrium diagram for the system chromium–water at 298 K, at relatively negative potential, pH 3.8 is the limit line between the corrosion and passivation regions of Cr.\(^{47}\)

Simultaneously, the hydrolysis of Fe\(^{2+}\) contributed to the penetration of chloride ions into the Cr compounds behind the rust layer, which caused the hydrolysis of Cr\(^{2+}\)\(^{38}\) and the localized pH decrease inside of the concentration cell.\(^{54-56}\) At a sufficiently low Cr content in the steel, H\(^+\) ions had sufficient time to diffuse partly into the bulk solution; therefore, the pH in the concentration cell was kept higher than 3.8. The Cr addition induced a beneficial effect on the corrosion protection of the 0.1 mass% Cr steel, 0.3 mass% Cr steel and the early stage of immersion of the 0.5 mass% Cr steel. However, the higher Cr content in the 0.5 mass% Cr steel at the advanced stage of immersion caused a decrease in the pH in the concentration cell lower than 3.8. This occurred easily as the bulk solution pH was 4. The autocatalytic process was therefore promoted, which activated the Cr and accelerated the propagation of localized corrosion.

4. Conclusions

(1) Potentiodynamic polarization tests, potentiostatic tests and EIS measurements formed a broad agreement in confirming the improvement in the corrosion behavior obtained by the addition of 0.1 and 0.3 mass% Cr, but not 0.5 mass% Cr, to blank steel. EIS measurements throughout 7-day continuous immersion revealed a relatively gradual increase in the steels’ corrosion rate.

(2) Localized corrosion (pitting corrosion) occurred on the surface of the steels after 10-h potentiostatic tests and after 7-day continuous immersion. Particularly, the 0.5 mass% Cr steel exhibited the heaviest corrosion.

(3) The addition of 0.1 and 0.3 mass% Cr promoted the formation of the beneficial Cu, Fe compounds, which were unable to form on the surface of the blank steel, and thereby enhanced the localized corrosion resistance. The over-alloying circumstance in the 0.5 mass% Cr steel lead to the negative effect of Cr addition due to the hydrolysis of metal chlorides. Finally, 0.3 mass% Cr addition was determined to be the optimum value for alloying to blank steel.

Acknowledgments

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