Electrochemical Behavior of Stainless Steel under High-Temperature and High-Pressure Methanol Solution Containing Oxygen and Chloride Ions

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Abstract: The effect of oxygen and water in a methanol solution containing 0.42 wt% LiCl on the corrosion behavior of Type 316L stainless steel was evaluated by anodic polarization and electrochemical impedance spectroscopy (EIS) at 423 K and 473 K. The $E_{\text{corr}}$ values in an aerated methanol solution decreased with immersion time and became almost the same as that observed in a deaerated methanol solution after 5 h. The dissolved oxygen molecules temporarily improved the corrosion resistance, judging from the increase in $E_a$ (anodic dissolution potential). This effect of oxygen molecules was not observed with the immersion time, consequently the anodic polarization curve became almost similar to that obtained in the absence of them. While the localized tarnish was observed in the aerated methanol solution with lower water contents, many pits formed when the water content increased. At 423 K, a corrosive effect of oxygen in the methanol solution was exhibited in the presence of water and pitting corrosion and autocatalytic reaction were observed. On the other hand, no corrosion occurred at 473 K, regardless of the oxygen and water concentrations.

Key words: Stainless steel, high temperature, high pressure, methanol, chloride ions, polarization curve, electrochemical impedance spectroscopy (EIS).

1. Introduction

Methanol has a lower critical point ($T_c$: 524 K, $P_c$: 8 MPa) than that of water ($T_c$: 647 K, $P_c$: 22 MPa), therefore, it provides advantages in terms of the design of chemical plants for the decomposition of harmful organics [1, 2], the organic synthesis [3], and the synthesis of alternative fuels [4]. Furthermore, the efficiencies of some chemical reactions are enhanced in a high-temperature methanol environment compared with that in supercritical water [5]. However, the leakage of the high-temperature and high-pressure methanol from reactors, could lead catastrophic accidents due to the high flammability of methanol. Therefore, the prevention of the unexpected leakages due to the corrosion of metals is one of the most important issues for the development of the industrial process using a high-temperature and high-pressure methanol.

Corrosion of metals in methanol solutions can be accelerated by the dissolved impurities such as water and oxygen molecules which are inevitably included in the reaction systems. Water, for example, can strongly affect the corrosion behavior of metals even when the concentration is very low. For instance, it is known that a small amount of water has a deleterious effect in a neutral solution, while passivating effect is observed in an acidic methanol solution [6]. Oxygen with 8 times higher solubility in methanol than that in water at 298 K [7] may also cause severe corrosion of

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metals in methanol solution, though unexpectedly smaller corrosion rates of iron [8] and zinc [9] in the aerated methanol solutions than those in the deaerated solutions have been reported.

In our previous studies, it has been revealed that the stainless steel and Ni-based alloy were passivated during immersion in both aerated and deaerated anhydrous methanol solutions above 423 K [10-13]. The passive films formed on the alloys have grown only in a deaerated methanol solution, based on the data of EIS and XPS analyses. The passive film did not grow in aerated methanol solution probably because the adsorbed oxygen layers on the metal surface acted as protective layers. In the presence of water, chloride attack was observed and an autocatalytic reaction of pitting corrosion occurs in the solutions containing water at higher concentrations, while the corrosion was suppressed at 473 K regardless of the presence of water and oxygen. However, the effect of oxygen on the corrosion behavior of metals in methanol containing water has not fully understood yet.

In this study, the effect of oxygen and water on the corrosion behavior of stainless steels and Ni-based alloy in a high-temperature and high-pressure methanol solution containing various concentrations of water was investigated by means of various electrochemical measurements.

2. Experimental Procedures

Reagent-grade methanol (99.8%, water content < 0.03%) and purified water (specific resistance of 18.2 MΩ·cm) were used as solvents. The test environment consisted of the mixture of methanol and water containing dry LiCl. The concentration of LiCl in the methanol solution was 0.42 wt%, and the water concentration was varied from 0.03 (anhydrous), 0.5 and 10 wt%. The electrolyte solution was bubbled either with air (aerated) or Ar gas (deaerated) before closing the cell. The pressure of the cell was increased by introducing Ar gas to reach 0.8 MPa and then the temperature started to increase.

All electrochemical measurements were carried out in a static autoclave made of Alloy C276 equipped with three electrodes, at 423 K and 473 K and under an over-pressure of 0.8 MPa. The alloy (for the working electrode) was type 316L stainless steel or Alloy C276 in a rod-type shape of 8 mm in diameter and 50 mm in length, which chemical composition was shown Table 1. The samples were abraded with water-proof emery paper (grit 600), immersed in a 30% nitric acid solution and then used as working electrodes. The treated electrodes were mounted in a tetrafluoroethylene-perfluoroalkylvinylether copolymer (PFA) sleeve sample holder except for an exposed test area of 2.0 cm². Prior to corrosion measurements, the exposed surfaces were polished again with water-proof emery paper (grit 600) in methanol. The counter electrode was a Pt wire. The reference electrode was an external pressure-balanced type silver/silver chloride (Ag/AgCl, at 298 K) electrode [14, 15]. The internal electrolyte was a pure methanol solution containing 0.42 wt% (0.1 mol/kg) LiCl. The liquid junction potential and electrode potential of Ag/AgCl in 0.42 wt% LiCl methanol solution against Ag/AgCl in 0.42 wt% aqueous solution at 298 K were 5mV and -60 mV, respectively. A maximum potential drop between the reference electrode and the working electrode was observed about 30 mV in anhydrous methanol solution for cell electrolyte solution, regardless of the temperature. The electrochemical measurements were carried out using anodic polarization, and electrochemical impedance spectroscopy (EIS). For Alloy C276, only anodic polarization measurement was performed in anhydrous solution. The anodic polarization

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 316L SS</td>
<td>0.016</td>
<td>0.28</td>
<td>1.16</td>
<td>0.035</td>
<td>0.015</td>
<td>Bal.</td>
<td>12.24</td>
<td>16.64</td>
<td>2.00</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Alloy C-276</td>
<td>0.0080</td>
<td>0.02</td>
<td>0.54</td>
<td>0.001</td>
<td>0.001</td>
<td>5.00</td>
<td>Bal.</td>
<td>14.98</td>
<td>15.91</td>
<td>3.29</td>
<td>1.00</td>
</tr>
</tbody>
</table>
measurements were initiated after 0.5-hour or 5-hour immersion. The potential was scanned from -50 mV with respect to $E_{corr}$ to a potential giving a current density of $10^{-3}$ A/cm$^2$ at the rate of 20 mV/min, and then the scanning direction was reversed. The anodic dissolution potential (hereafter $E_a$) was defined as the potential at which the current density reached $10^{-4}$ A/cm$^2$. After the measurements, the electrodes were examined with an optical microscope.

EIS measurements were conducted every hour during a 5-hour immersion. A sine wave with low amplitude of ±5 mV was superimposed on the corrosion potential $E_{corr}$ in the frequency range between 10 kHz and 10 mHz.

3. Results

3.1 Effect of the Dissolved Oxygen on the Anodic Polarization

The effect of dissolved oxygen on the electrochemical behavior in a high-temperature and a high-pressure methanol solution was evaluated in an aerated solution. Fig. 1 shows the variation of $E_{corr}$ during immersion and the polarization curves of Type 316L SS and Alloy C276 in 0.42 wt% LiCl methanol solution at 423 K. The polarization curves obtained in the deaerated methanol solution were also shown with
dotted lines in Fig. 1, which was reported in our previous paper [10]. During the anodic scan, no passive region was observed in the curves of Type 316L SS both after 0.5- and 5-h immersion. It should be noted that the $E_{\text{corr}}$ and $E_a$ values obtained in an aerated solution were more positive than those observed in a deaerated solution, and they shifted to a negative direction when the sample was immersed longer. A similar behavior except for the shift of $E_a$ was observed for Alloy C276 in aerated methanol solution.

Fig. 2 shows the variation of $E_{\text{corr}}$ and anodic polarization curves of Type 316L SS and Alloy C276 in 0.42 wt% LiCl methanol solution at a higher temperature of 473 K. The $E_{\text{corr}}$ and $E_a$ values changed more rapidly than those at 423 K. The $E_{\text{corr}}$ shifted to lower potentials accompanied by a long-term oscillation with frequencies of approximately 20-40 min$^{-1}$, regardless of the alloy types. The $E_{\text{corr}}$ of Alloy C276 started to shift rapidly to a negative direction at 2.5 h and became almost constant value with smaller amplitudes, and this value was almost the same as that observed in a deaerated methanol solution as shown with dotted lines. Furthermore, an anodic polarization curve of Alloy C276 after 5-hour immersion was very similar to that obtained in a deaerated methanol solution.

3.2 Effect of Water on the Anodic Polarization in Aerated Solution

The effect of water on the electrochemical behavior of Type 316L SS in an aerated methanol solution was evaluated. Fig. 3 shows the anodic polarization curves of Type 316L SS in the aerated methanol-water
mixtures at 423 and 473 K. At 423 K, the effect of water on the electrochemical behavior was not apparent and all polarization curves have no passive region. On the other hand, the regions of lower current density around $10^{-5}$ mA/cm$^2$ which may be regarded as passive region were observed, considering that the passive current density increased with increase in temperature [16, 17]. It was more apparently observed at a higher temperature of 473 K even in the solution containing 0.5% of water, and this region became wider when the water content increased.

3.3 Surface Morphology

The optical images of Type 316L SS after anodic polarization measurements at 423 K in the presence and absence of water are shown in Fig. 4. In the absence of water, localized tarnish was observed and this was almost the same as that observed for the sample polarized in a deaerated solution shown in our previous study [10]. However, when 0.5% of water was added, pitting was observed instead of the localized tarnish. This is in contrast with the results obtained in a deaerated solution where the localized tarnish was commonly observed until the concentration of water reached 1.5% [12].

3.4 EIS Study of the Corrosion

The corrosion behavior of Type 316L SS in the
aerated methanol-water mixture was investigated by EIS. Nyquist plots of Type 316L SS in the aerated methanol containing 0.5% of water at 423 K are shown in Fig. 5. The obtained impedance plots exhibited clear semi-circle. The diameters of the semi-circles increased while the phase degree shifts were almost constant until 2 h of immersion, which indicates the passive state of Type 316L SS. The

Fig. 5 Nyquist plots with time for Type 316L SS immersed in 0.42 wt% LiCl aerated methanol-0.5% water mixtures at 423 K.
initiation of corrosion was observed after 3 h of immersion, judging from the remarkable decrease in \( R_p \) (semi-circle diameter) and phase shifts. The corrosion rate seems almost constant based on the observation of clear semi-circle. After 4 h of immersion, the gradual increase in \( R_p \) indicates the reduced corrosion rate.

Nyquist plots of Type 316L SS in the aerated methanol containing 10% of water at 423 K are shown in Fig. 6. The impedance plots from 0 to 2 h of immersion exhibited clear semi-circle, and the decrease in \( R_p \) was observed immediately after immersion. The corrosion initiated after 2 h of immersion, based on the significant decrease in \( R_p \) and phase degree shift. At the same time, the \( E_{\text{corr}} \) steeply dropped to -875 mV. After 3 and 4 h of immersion, the values of impedance became smaller and scattered, exhibiting too fast corrosion dynamics during this measurement duration. This scattered impedance plots suggest the fast progression of pitting corrosion, leading so-called autocatalytic reaction [18]. After 5 h of immersion, a semi-circle was again observed which indicated the reduced rate of pitting corrosion probably caused by the formation of some deposit layers.

Nyquist plots of Type 316L SS in the aerated methanol containing water at 473 K are shown in Fig. 7. Stable semi-circles were observed during immersion regardless of the water contents, no significant decrease in \( R_p \) and phase shift was observed during immersion, suggesting that rapid corrosion did not occur in the aerated methanol containing both 0.5% and 10% of water at 473 K.

Fig. 6  Nyquist plots with time for Type 316L SS immersed in 0.42 wt% LiCl aerated methanol-10% water mixtures at 423 K.
4. Discussion

4.1 Cathodic Reaction of Oxygen

Based on the results, it has been clarified that both oxygen and water molecules give great influence on the corrosion of metals in the methanol solutions containing chloride ions at high temperatures under a high pressure. Especially, the cathodic reaction of oxygen molecules has different behavior under the presence of water in methanol solution.

In the absence of water, the rate of cathodic reaction is expected very slow. If the cathodic reaction has same rate in water, a severe corrosion occurs in methanol solution due to the solubility of oxygen in methanol is higher than that in water (for example, 0.227 and 0.027 cm$^3$/cm$^3$ at 1 atom and 298 K, respectively [7]). As the results, the slow cathodic reaction induces the shifts of $E_a$ to positive direction observed in an anhydrous methanol and indicating the improvement of corrosion resistance. The shift of $E_a$ should be caused by the formation of temporal oxygen layer on metal surface in the process of the slow cathodic reaction.

4.2 Growth of Passive Film

The shift of $E_{corr}$ to negative direction with immersion period was accompanied by a long-term oscillation and it finally reached the same values as those observed in a deaerated solution, indicating the decrease in the effect of oxygen as the increase in immersion time. A similar potential oscillation is reported in a conc. sulfuric acid solution, in which dissolution and regeneration of metal sulfate was alternatively occurred on the surface of the metal [19-24]. In our previous paper, we have suggested that the oxygen adsorption layer prevents the corrosion of metals. The present results indicate that these adsorbed oxygen molecules are consumed most likely according to the cathodic reaction during immersion and the oxidation of metals is accompanied. The precipitation and dissolution of the formed metal methoxides [25] and hydroxides are alternatively occurred at a low rate, causing the long-term potential oscillation. After most of the dissolved oxygen molecules are consumed, the potential reaches the same value as that observed in a deaerated solution. At higher temperatures, the rate of cathodic reaction should be relatively higher, therefore, the change of the $E_{corr}$ was faster. This scenario also well explains the fact that the passivating film did not grow based on the EIS measurements and our previous XPS study [11].
4.3 Effect of Water on Corrosion

On the other hand, in the presence of water, the cathodic reaction which is a very fast process can occur, as suggested by the more rapid change in the $E_{\text{corr}}$ during EIS measurements shown in the inset of Figs. 5-7. The ratio of the resulting metal hydroxide and metal methoxide as well as the properties of them should be changed depending on the concentration of water and temperature, which can affect the corrosion behavior of metals. EIS measurements indicated that 316L SS was more severely corroded after immersed for 3 or 4 h at 423 K in methanol containing 10% of water. This indicates that the contribution of hydroxide film was more significant on the morphology of corrosion and the activity.

5. Conclusions

The $E_{\text{corr}}$ of alloys shifted to negative direction during immersion of them in an anhydrous methanol solution even containing oxygen, and accelerating the shift at higher temperature.

The $E_a$ of alloys shifted to positive direction temporarily in an anhydrous methanol solution, indicating the improved corrosion resistance.

Addition of water in aerated methanol solutions accelerated the chloride attack, and autocatalytic reaction was induced in the solution with a higher water concentration of 10%.

No corrosion of Type 316L SS occurred at 473 K in the methanol solution despite of the presence of water and oxygen.

The role of oxygen as reduction reagent to corrosion is weak in anhydrous methanol solution.

References


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