Influence of Cu on the Passivation Behavior of Fe-20Cr-xCu (x = 0, 2, 4 wt%) Alloys in Sulfuric Acid Solution

KkochNim Oh,* Ihsan-ul-Haq Toor,** SooHoon Ahn,* and HyukSang Kwon‡,*

ABSTRACT

Effects of Cu on the polarization behavior of Fe-20Cr-xCu (x = 0, 2, 4 wt%) were examined in deaerated 0.1 M sulfuric acid (H2SO4) solution. In the active region, corrosion resistance of the alloys is improved with Cu content as a result of the enrichment of Cu on the surface of the alloys that occurs by the preferential dissolution of Fe. In the passive region, the effects of Cu on the passivation behavior of the alloys was dependent on the applied potential. At potentials active to −100 mV vs. saturated calomel electrode (SCE), the passivity of the alloys is improved with Cu content, which is confirmed by the increase in passivation rate with a decrease in oxidation tendency. In contrast, above −100 mV SCE, where the oxidation reaction of Cu+ to Cu2+ occurs, the passivity of the alloys was degraded significantly with Cu content, as confirmed by the increase in passive current density as well as the significant decrease in passivation rate. The deleterious effects of Cu on the passivation behavior of Fe-20Cr-xCu (x = 0, 2, 4 wt%) decreased at potentials noble to 500 mV SCE, primarily as a result of the significant decrease in Cu content in passive film and hence of the decrease in the oxidation reaction of Cu+ to Cu2+.

KEY WORDS: acid, corrosion, copper, passivation, passivity

INTRODUCTION

Stainless steels have been used extensively in many different industrial applications because of their excellent corrosion resistance and good mechanical properties. Passive films on stainless steels are responsible for their excellent corrosion resistance in different environments, and so it is important to investigate the effects of different alloying elements on the passive film structure and composition. There have been many studies that showed that the passive films on stainless steels consist of Cr-enriched (Fe, Cr) oxide/hydroxide, although there is still some controversy as to the detailed structure and composition of the passive films.

Cu is used widely as an alloying element for improving the corrosion resistance of stainless steels in acidic environments, because it has been reported that Cu suppresses the anodic dissolution by its enrichment on the surface of the alloys.1-7 However, stainless steels containing Cu show the second anodic current peak in the passive region, in addition to the critical anodic current peak (Ic) in the active region.3,7,8 Davies claimed that the peak is related to the oxidation of adsorbed hydrogen atoms formed during the anodic polarization in an acidic solution.8 On the other hand, Seo, et al., reported that the peak is from the dissolution of the Cu layer deposited on the surface of stainless steels.3 Some others found that Cu has a positive effect on the passivation of stainless steels in an acidic solution;5,10-11 however, Lizlovs claimed that Cu has a detrimental effect on passivation.1

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The inconsistencies in the reported results by various researchers were mainly due to the fact that most of stainless steels used for the investigation had many different alloying elements including Cu, so it was difficult to elucidate the independent effects of Cu on the polarization behavior in the stainless steels. Therefore, the objective of this study was to investigate the independent effects of Cu on the existence of the second anodic current peak and polarization behavior of Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys in acidic solution.

EXPERIMENTAL PROCEDURES

Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys were prepared by vacuum arc melting, and then cast in the form of button. The cast was homogenized for 120 min at 1,200°C and then hot-rolled into a 3 mm thick plate. The specimens were prepared by cold-rolling the hot-rolled plates into 1.6 mm thick sheets, solution-annealing for 30 min at 1,050°C, followed by water-quenching. The chemical composition of the alloys is given in Table 1. For electrochemical tests, specimens were prepared using 1500-grit silicon carbide (SiC) paper subsequently polished using alumina (Al₂O₃) paste and then ultrasonically cleaned with ethanol (C₂H₆O).

Potentiodynamic polarization tests were conducted in deaerated 0.1 M sulfuric acid (H₂SO₄) solution at 30°C to examine the effects of Cu on the polarization behavior of Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys. The electrochemical cell for the tests was equipped with a platinum counter electrode, a saturated calomel reference electrode (SCE), and a test specimen as a working electrode. Polarization curves of the alloys were measured in the noble direction from ~800 mV SCE at a scan rate of 1 mV/s after a cathodic cleaning for 100 s at ~800 mV SCE. Polarization testing on each alloy was conducted three times, and then the polarization curve showing average polarization behavior was selected for presentation in this work.

Chemical analysis by x-ray photoelectron spectroscopy (XPS) was conducted on the surface of the Fe-20Cr-4Cu alloy after being held in the active region at corrosion potential (Ecorr) and after being polarized up to various potentials (~200 mV SCE, 100 mV SCE, 300 mV SCE, and 500 mV SCE) in the passive region from Ecorr in 0.1 M H₂SO₄ solution. The XPS measurements were performed using the monochromatic Al-Kα x-ray source (15 kV, 20 mA, 300 W) and a pass energy of 20 eV. The reference energies were the C1s signal at 284.5 eV and the O1s signal at 531.0 eV. XPS spectra were analyzed using an XPS analysis software, and 80% Lorentzian-Gaussian fits were used in the entire XPS spectra curve fitting.

To examine the effects of Cu content and applied potential on the passivation rate of the Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys, preexisted passive film of the alloys were initially removed by cathodic cleaning for 200 s at ~680 mV SCE in deaerated 0.1 M H₂SO₄ solution, and then the applied potential was shifted instantly to a potential in the passive region, followed by measuring current transient.

RESULTS AND DISCUSSION

Polarization Behavior—Active Region

Figure 1 shows the polarization behavior of Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys in deaerated 0.1 M H₂SO₄ solution at 30°C. The addition of Cu to Fe-20Cr alloy increased the cathodic current density and the Ecorr in the noble direction, whereas the Ic decreased significantly with an increase in Cu content of the alloys. It appears that the shift of the Ecorr in the noble direction, the increase in the cathodic current density, and the significant decrease in the Ic are associated with the change in alloy composition on the surface of the alloys in the acidic solution. It is evident from Table 2 that the surface of Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys that have been subjected to cathodic cleaning for 100 s at ~800 mV SCE and then to initial exposure to solution at open circuit for 15 min before the polarization test is enriched with Cu primarily because of a selective dissolution of a more
TABLE 2

Chemical Compositions (wt%) on the Surface of Fe-20Cr-xCu Alloys That Have Been Exposed for 15 min to Deaerated 0.1 M H2SO4 Solution at Ecor, Analyzed Using Energy-Dispersive Spectroscopy

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Fe (wt%)</th>
<th>Cr (wt%)</th>
<th>Cu (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-20Cr</td>
<td>78.23</td>
<td>21.77</td>
<td></td>
</tr>
<tr>
<td>Fe-20Cr-2Cu</td>
<td>67.23</td>
<td>25.46</td>
<td>7.31</td>
</tr>
<tr>
<td>Fe-20Cr-4Cu</td>
<td>62.80</td>
<td>25.77</td>
<td>11.43</td>
</tr>
</tbody>
</table>

FIGURE 2. Effects of applied potential on the Cu content on the surface of Fe-20Cr-4Cu alloy that has been polarized to the specific potential from Ecor in deaerated 0.1 M H2SO4 solution at 30°C. The average Cu contents were measured based on the XPS data on the surface of the alloys.

active element such as Fe in the solution. Hence, the increase in Ecor, and the cathodic current density, and the significant decrease in I, with Cu content for the Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys, were primarily from the Cu enrichment on the surface of the alloys.

Polarization Behavior—Passive Region

In the passive region, the passive current density (ip) of Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys increased with its Cu content as shown in Figure 1. In the Cu-containing alloys (Fe-20Cr-2Cu and Fe-20Cr-4Cu), the increase in the passive current density was observed at potentials noble to –100 mV SCE, which has been explained by the oxidation of adsorbed hydrogen atoms formed during cathodic polarization or by the dissolution of Cu on the alloy surface. Figure 2 shows the Cu content measured on the surface of the Fe-20Cr-4Cu alloy that has been polarized at Ecor and to –200 mV SCE, 0 mV SCE, 100 mV SCE, 300 mV SCE, and 500 mV SCE, respectively, in deaerated 0.1 M H2SO4 solution at 30°C. Evidently, the surface of the Fe-20Cr-4Cu alloy is enriched heavily (30.4 at%) with Cu at Ecor, or in an active state, and the Cu content increased further to 38.2 at% during the anodic polarization up to –200 mV SCE, probably as a result of the selective dissolution of Fe in the active region. However, above the potential (–200 mV SCE), the Cu content was decreased gradually with the increase in potential presumably from the dissolution of Cu on the surface of Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys, as confirmed by the increase in passive current density in the polarization curves in Figure 1.

The potential, –100 mV SCE, at which the passive current density starts to increase in the passive region (as shown in Figure 1) is very close to the standard electrode potential between Cu+ and Cu2+ species (ECu2+/Cu+ = –88 mV SCE). The electrode potential for the equilibrium reaction (Equation [1]) between Cu+ and Cu2+ is shown in Equation (2): 14

\[ \text{Cu}^2+ + \text{e}^- = \text{Cu} \]  
(1)

\[ E_{\text{Cu}^2+/\text{Cu}^+} = –88 \pm 59.1 \log([\text{Cu}^2+]/[\text{Cu}^+]) \text{ (mV SCE)} \]  
(2)

According to Equation (1), the increase in passive current density at potentials noble to approximately –100 mV SCE in Figure 1 is attributed to the oxidation of Cu+ to Cu2+. However, the source of Cu+ is not clear. Hence, Cu-XPS spectra for the passive films on Fe-20Cr-4Cu alloy polarized to –200, 0, 100, 300, and 500 mV SCE, respectively, were analyzed using an XPS analysis software and are presented in Figure 3.

Table 3 shows average Cu2p3/2 binding energy and FWHM (full width at half maximum) of the Cu-XPS spectra on the surface of the Fe-20Cr-4Cu alloy at each potential based on the assumption that only one Cu chemical bond exists (before the Cu-XPS spectra fitting shown in Figure 3). Both average Cu2p3/2 binding energy and FWHM of the Cu-XPS spectra at 100 mV SCE are quite different from those of Cu-XPS spectra at –200 mV SCE and 0 mV SCE, while they are similar to those of Cu-XPS spectra at 300 mV SCE and 500 mV SCE. Considering that the change in the Cu-XPS spectra from –200 mV SCE to 500 mV SCE is a result of continuous reactions of Cu with solution on the surface of the Fe-20Cr-4Cu alloy, hence both the shift in Cu2p3/2 binding energy and the increase in FWHM (relatively broad) with an increase in the potential from 0 mV SCE to 100 mV SCE, suggest that another Cu chemical bond might exist at potentials noble to 100 mV SCE. Moreover, there is a shoulder at approximately 933 eV of Cu2p3/2 binding energy as shown in Figures 3(c), (d), and (e). Therefore, the Cu-XPS spectra curve fitting was performed by an XPS analysis software based on the two Cu chemical bonds at potentials noble to 100 mV SCE and these chemical bonds are associated with those in metallic Cu, cuprous oxide (Cu2O), and cupric oxide (CuO), respectively. Especially the blue-colored Cu-XPS peak in Figure 3(c) or the main gist in the Cu-XPS spectra
has lower binding energy than that of the green-colored Cu-XPS peak; hence, the green-colored spectrum is from CuO, whereas the blue-colored Cu-XPS spectrum is from Cu$_2$O and/or metallic Cu. However, it is very difficult to separate the Cu-XPS spectrum of metallic Cu from that of Cu$_2$O accurately, since their binding energies are too close. According to Ghijsen, et al., the binding energies of metallic Cu and Cu$_2$O are 932.3±0.1 eV and 932.4±0.2 eV, respectively; the difference between them is only 0.1 eV. Hence, it is very difficult to clarify the Cu chemical bond of the blue-colored Cu-XPS spectrum in Figure 3. However, it was reported that Cu-XPS spectrum associated with metallic Cu can be differentiated from that with Cu$_2$O using a Cu-LMM x-ray-induced Auger peak, which primarily is from the relatively large difference in the kinetic energy of the Cu-LMM Auger peak between metallic Cu and Cu$_2$O; the kinetic energy of the Cu-LMM Auger peak for metallic Cu and that for Cu$_2$O are 918 eV and 916 eV, respectively. Figure 4(a) shows the XPS depth profile of Fe-20Cr-4Cu alloy that has been polarized to ~200 mV$_{SCE}$ from $E_{corr}$ at a scan rate of 1 mV/s. (b) XPS spectra over the wide range of kinetic energy including all alloying elements before and after 1,000 s etching for measuring XPS depth profile.

### TABLE 3

<table>
<thead>
<tr>
<th>Potential (mV$_{SCE}$)</th>
<th>Binding Energy (eV)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–200</td>
<td>932.58±0.01</td>
<td>1.38±0.02</td>
</tr>
<tr>
<td>0</td>
<td>932.59±0.01</td>
<td>1.41±0.01</td>
</tr>
<tr>
<td>100</td>
<td>932.67±0.02</td>
<td>1.47±0.02</td>
</tr>
<tr>
<td>300</td>
<td>932.70±0.01</td>
<td>1.50±0.01</td>
</tr>
<tr>
<td>500</td>
<td>932.67±0.02</td>
<td>1.48±0.01</td>
</tr>
</tbody>
</table>

**FIGURE 3.** Cu-XPS spectra on the surface of Fe-20Cr-4Cu alloy that has been polarized to the specific potential from $E_{corr}$ in deaerated 0.1 M H$_2$SO$_4$ solution at 30°C: (a) –200 mV$_{SCE}$; (b) 0 mV$_{SCE}$; (c) 100 mV$_{SCE}$; (d) 300 mV$_{SCE}$; and (e) 500 mV$_{SCE}$.

**FIGURE 4.** (a) XPS depth profile of Fe-20Cr-4Cu alloy that has been polarized to ~200 mV$_{SCE}$ from $E_{corr}$ at a scan rate of 1 mV/s. (b) XPS spectra over the wide range of kinetic energy including all alloying elements before and after 1,000 s etching for measuring XPS depth profile.
elements before and after 1,000 s etching for measuring XPS depth profile. Further, XPS spectra showing the Cu-LMM Auger peak near 916 eV before and after the 1,000 s etching are shown, respectively, in the inset of Figure 4(b). Evidently, in the inset, the Cu-LMM Auger peak at 916 eV, which originated from Cu$_2$O, is shown only in the XPS spectra measured before etching or on the surface of the film formed on the alloy. In contrast, the Cu-LMM Auger peak at 918 eV originated from the metallic Cu appeared only in the spectra measured after 1,000 s etching. Hence, the blue-colored XPS spectrum in Figure 3 that is measured on the surface of the passive film without etching is originated from Cu$_2$O. Peak shift in the Cr$_{2p3}$ Cr-XPS peak also was observed due principally to the phase transform from an oxide to a metal during depth profile, and the intensity of the peak was increased because of the increase in Cr content as shown in Figure 4(a). However, comparing the escape depth (5 nm) of photoelectrons$^{15}$ with the thickness (2.5 nm to ~4 nm)$^{20-23}$ of passive films formed on stainless steel, a small amount of the Cu-XPS spectrum originated from metallic Cu beneath the passive film may be included in the blue-colored Cu-XPS spectrum in Figure 3. However, it is difficult to separate these Cu chemical bonds from each other using an XPS analysis software, and hence Cu$_2$O, which is a main part of the Cu chemical bond of the blue-colored Cu-XPS spectrum in Figure 3, was taken in this study.

Figure 3 shows the results of the Cu-XPS spectra curve fitting at each potential. For the Cu-XPS spectra curve fitting at –200 mV$_{\text{SCE}}$ and 0 mV$_{\text{SCE}}$, as shown in Figures 3(a) and (b), Cu$_2$O (932.6 eV)$^{24}$ was taken since the binding energy of Cu$_2$P$_{3/2}$ at –200 mV$_{\text{SCE}}$ and 0 mV$_{\text{SCE}}$ is almost 932.6 eV as shown in Table 3. For the Cu-XPS spectra curve fitting at potentials noble to 100 mV$_{\text{SCE}}$, both Cu$_2$O (932.4 eV)$^{24}$ and CuO (933.2 eV)$^{16}$ were selected as shown in Figures 3(c), (d), and (e). The shift of Cu$_2$O binding energy from 932.6 eV at potentials below 0 mV$_{\text{SCE}}$ to 932.4 eV at potentials above 100 mV$_{\text{SCE}}$ is primarily because of the existence of a new Cu chemical bond such as CuO. Ghijsen, et al.$^{16}$ have reported that Cu$_2$O has a binding energy of 932.4 ± 0.2 eV while that of CuO has 933.2 ± 0.2 eV. In this study, 932.4 eV (Cu$_2$O) and 933.2 eV (CuO) were used as binding energies for each copper oxide, and then the Cu-XPS spectra curve fitting at potentials noble to 100 mV$_{\text{SCE}}$ was performed based on the two oxides. Table 4 presents average binding energy and FWHM of the fitted Cu-XPS spectra such as Cu$_2$O and CuO at each potential as shown in Figure 3.

It is evident from the Cu-XPS spectra of the Fe-20Cr-4Cu alloy at –200 mV$_{\text{SCE}}$. In Figure 3(a) that the source of Cu$^+$ in Equation (1) was from Cu$_2$O (932.6 eV)$^{24}$. The equilibrium reaction between Cu$_2$O and Cu$^+$ and the corresponding relationship between [Cu$^+$] and pH are expressed by Equations (3) and (4), respectively.$^{14}$ Equation (3) is not an electrochemical reaction, but simply a chemical reaction, so Cu$^+$ is formed from Cu$_2$O at the interface between the oxide film and the solution at potentials below –100 mV$_{\text{SCE}}$ in the passive region. The adsorbed Cu$^+$ on the surface of the Fe-20Cr-4Cu alloy oxidized to Cu$^{2+}$ according to Equation (1). It is evident from Figure 3(b) that the intensity of Cu$_2$O or the source of Cu$^+$ was decreased significantly at 0 mV$_{\text{SCE}}$ compared with that at –200 mV$_{\text{SCE}}$ shown in Figure 3(a). Therefore, the increase in the passive current density observed at potentials noble to –100 mV$_{\text{SCE}}$ was primarily from the oxidation reaction of Cu$^+$ to Cu$^{2+}$.

$$\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Cu}^+ + \text{H}_2\text{O}$$  (3)

$$\text{log}[\text{Cu}^+] = 0.84 - \text{pH}$$  (4)

The intensity of the Cu$_2$O peak at 100 mV$_{\text{SCE}}$ was decreased further compared with that at 0 mV$_{\text{SCE}}$ by the oxidation reaction of Cu$^+$, as confirmed in Figure 3(c). However, Cu$_2$O (933.2 eV)$^{16}$ and CuO (934.2 eV)$^{16}$ were observed at a potential of 100 mV$_{\text{SCE}}$. CuO can be formed from either Cu$_2$O in film or a dissolved substance (Cu$^+$) by the electrochemical reaction.$^{14}$ However, the standard electrode potentials (E$_{\text{Cu}_2\text{O}/\text{CuO}} = 428$ mV$_{\text{SCE}}$, E$_{\text{Cu}^+/\text{CuO}} = 379$ mV$_{\text{SCE}}$) are so high that CuO cannot be formed at quite low potentials such as 100 mV$_{\text{SCE}}$ by an electrochemical reaction. However, CuO is formed via a chemical reaction when Cu$^{2+}$ accumulated on the Cu surface reacts with water, as represented in Equation (5).$^{14}$

$$\text{Cu}^{2+} + \text{H}_2\text{O} \rightarrow \text{CuO} + 2\text{H}^+$$  (5)

$$\text{log}[\text{Cu}^{2+}] = 7.89 - 2\text{pH}$$  (6)

The Cu-XPS spectra (Figure 3[d]) for the film formed at 300 mV$_{\text{SCE}}$ shows Cu chemical bonds for Cu$_2$O and CuO. However, the average Cu content (Figure 2) or the intensity of the Cu-XPS spectra for the passive film formed at 300 mV$_{\text{SCE}}$ was decreased slightly as compared with that at 100 mV$_{\text{SCE}}$. More-

<table>
<thead>
<tr>
<th>Potential (mV$_{\text{SCE}}$)</th>
<th>Cu$_2$O (eV)</th>
<th>CuO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BE (eV)</td>
<td>FWHM (eV)</td>
</tr>
<tr>
<td>–200</td>
<td>932.6</td>
<td>1.39±0.02</td>
</tr>
<tr>
<td>0</td>
<td>932.6</td>
<td>1.41±0.01</td>
</tr>
<tr>
<td>100</td>
<td>932.4</td>
<td>1.09±0.02</td>
</tr>
<tr>
<td>300</td>
<td>932.4</td>
<td>1.14±0.01</td>
</tr>
<tr>
<td>500</td>
<td>932.4</td>
<td>0.9±0.02</td>
</tr>
</tbody>
</table>
over, the current density in the polarization behavior of Fe-20Cr-4Cu alloy in Figure 1 decreased drastically from 100 mV\textsubscript{SCE} to 300 mV\textsubscript{SCE}, while that of the current density increased significantly from –100 mV\textsubscript{SCE} to 100 mV\textsubscript{SCE}. The increase in the current density from –100 mV\textsubscript{SCE} to 100 mV\textsubscript{SCE} is a result of the oxidation of Cu\textsuperscript{+} to Cu\textsuperscript{2+} according to Equation (1). Therefore, the intensity of Cu\textsubscript{2}O or the source of Cu\textsuperscript{+} decreased considerably from –200 mV\textsubscript{SCE} to 100 mV\textsubscript{SCE} as confirmed in Figures 3(a), (b), and (c), while it decreased slightly from 100 mV\textsubscript{SCE} to 300 mV\textsubscript{SCE}. However, the decrease in the current density in the polarization behavior of Fe-20Cr-4Cu alloy observed from 100 mV\textsubscript{SCE} to 300 mV\textsubscript{SCE} in Figure 1, presumably as a result of the decrease in the reaction rate of Equation (1) with an increase in the potential, is a result of reduction in [Cu\textsuperscript{+}] on the surface of Fe-20Cr-4Cu alloy. According to Equations (3) and (4), directly related to Equation (1), the decrease in [Cu\textsuperscript{+}], which causes the decrease in the reaction rate of Equation (1), is caused primarily by the increase in pH value because of H\textsuperscript{+} ions’ consumption at the surface of the Fe-20Cr-4Cu alloy since Equation (3) occurs drastically from –100 mV\textsubscript{SCE} to 100 mV\textsubscript{SCE}. Hence, the intensity of Cu\textsubscript{2}O was decreased slightly from 100 mV\textsubscript{SCE} to 300 mV\textsubscript{SCE} because of the decrease in the reaction rate of Equation (3), as a result of the increase in pH value at the surface of Fe-20Cr-4Cu alloy.

Figure 3(e) presents the Cu-XPS spectra for the passive film formed on the Fe-20Cr-4Cu alloy polarized at 500 mV\textsubscript{SCE}. The intensity for the chemical bonds of Cu\textsubscript{2}O and CuO reduced almost to zero. At the potential, Cu\textsubscript{2}O in the film would be dissolved completely into the solution via Equation (7), and CuO also was dissolved in acid solution according to Equation (5) when there was not any source available for Cu\textsuperscript{2+} accumulation.\textsuperscript{14}

\begin{equation}
\text{Cu}_2\text{O} + 2\text{H}^+ = 2\text{Cu}^{2+} + \text{H}_2\text{O} + 2\text{e}^- \tag{7}
\end{equation}

\begin{equation}
E_{\text{Cu}_2\text{O}/\text{Cu}^{2+}} = -38 + 59 \log[\text{Cu}^{2+}] \text{ [mV}_{\text{SCE}] \cdot \text{pH} 2} \tag{8}
\end{equation}

**Passivation Rate**

As shown in Figure 1, the Cu-containing alloys (Fe-20Cr-2Cu and Fe-20Cr-4Cu) exhibited higher passive current density than the Fe-20Cu alloy at potentials noble to –100 mV\textsubscript{SCE}. Therefore, the passive region on these alloys is divided into two parts: passive region I (below –100 mV\textsubscript{SCE}) and passive region II (above –100 mV\textsubscript{SCE}). The XPS results presented in the previous section showed that the increase in passive current density in passive region II was related to the oxidation of Cu\textsuperscript{+} and Cu\textsubscript{2}O in the passive film. Here, in this section, effects of Cu content on the passivation rate of the alloys in the passive regions I and II will be presented.

**FIGURE 5.** Current transient curves of Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys in deaerated 0.1 M H\textsubscript{2}SO\textsubscript{4} solution at 30°C when the potential of each alloy was switched from –680 mV to the specific potentials: (a) –300 mV\textsubscript{SCE}, (b) 100 mV\textsubscript{SCE}, and (c) 400 mV\textsubscript{SCE}. The preexisted oxide films of the alloys were removed initially by cathodic cleaning for 100 s at –680 mV\textsubscript{SCE} in deaerated 0.1 M H\textsubscript{2}SO\textsubscript{4} solution.

Figure 5 shows the current transient curves of Fe-20Cr-xCu (x = 0, 2, 4 wt%) alloys when the applied potential was switched to the passivation potentials (–300, 100, and 400 mV\textsubscript{SCE}) from –680 mV\textsubscript{SCE} in deaerated 0.1 M H\textsubscript{2}SO\textsubscript{4} solution at 30°C, where the alloy
had been cathodically cleaned to remove completely any oxide films formed on the alloys in air. When the applied potential was switched to the passivation potential, the anodic current increased abruptly to the peak value as a result of oxidation of the alloys, and then decreased as passivation occurred. The peak current density of the alloy increased with passivation potential because of the increase in oxidation tendency of the alloys. The time taken for the passivation current to be decreased to the predetermined value of 0.05 mA/cm² for each alloy were measured and counted as a passivation time. The shorter the passivation time, the faster is the passivation rate of the alloy. The results are presented in Table 5.

At ~300 mV_{SCE} (Figure 5(a)), the peak current density and passivation time decreased with an increase in Cu content of the alloys, confirming that for the alloys in passive region I, the increase in Cu content increased the passivation rate with a decrease in oxidation tendency. As reported previously, the passivation rate of a metal or alloy is inversely related to its passivation rate. The factors affecting the value of Ic,5,25-26 and hence, the influence of Cu on the passivation behavior depends on the applied potential. In passive region I or at potentials active to about ~100 mV_{SCE}, the passivation rate decreases with Cu content as a result of the oxidation of Cu⁺ and Cu₂O to Cu²⁺.

CONCLUSIONS

- The addition of Cu to Fe-20Cr alloy is beneficial in improving the corrosion resistance of the alloys in the active region, as confirmed by the increase in Ic, primarily caused by the enrichment of Cu on the surface in the alloys.
- In the passive region, the influence of Cu on the passivation behavior depends on the applied potential. In passive region I or at potentials active to about ~100 mV_{SCE}, the decrease in oxidation tendency, as shown in Figure 5(b), the passivation rate of the alloys decreased with Cu content as a result of the oxidation of Cu⁺ and/or Cu₂O to Cu²⁺.

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