

# Effect of alloying Copper on the Corrosion Resistance of Stainless Steels in Chloride Media

T. Ujiro, S. Satoh, R.W. Staehle\*, and W.H. Smyrl\*

*Technical Research Laboratories, Kawasaki Steels Corp.,  
1 Kawasaki-cho, Chuo-ku, Chiba 260, JAPAN*

*\*Corrosion Research Center, Department of Chemical Engineering and  
Materials Science, University of Minnesota*

*112 Amundson Hall, 221 Church Street SE, Minneapolis, Minnesota 55455, USA*

In order to explain the effect of alloying Cu on the corrosion resistance of stainless steels in chloride media for both ferritic and austenitic stainless steels, the corrosion behavior of Cu-bearing stainless steels was investigated. Alloying Cu showed beneficial effect in an active potential range and harmful effect in a noble potential range. The beneficial effect of alloying Cu was explained by the stability of deposited Cu on an anodic surface. Difference in the effect of alloying Cu between the ferritic and austenitic steels was ascribed by the differences in their corrosion potentials and the morphology of the deposited Cu.

**Keywords** : stainless steel, copper, chloride media, localized corrosion, corrosion potential

## 1. Introduction

Copper (Cu) is a well-known alloying element that is used to improve the resistance to general corrosion of stainless steels.<sup>1)-5)</sup> However, the effect of alloying Cu on the resistance to localized corrosion of stainless steels in chloride media has not been clarified sufficiently. As long as localized corrosion is concerned, the research in the effect of alloying Cu has much contradiction between ferritic and austenitic stainless steels. In the case of austenitic stainless steels, some researchers<sup>6),7)</sup> reported that alloying Cu had a harmful effect on the corrosion rate and pitting potential in chloride media. Other researchers<sup>7)-10)</sup> reported that alloying Cu had a beneficial effect on the corrosion rate, crevice corrosion potential, and pitting protection potential. On the other hand, alloying Cu always improved the resistance to localized corrosion of ferritic stainless steels.<sup>11),12)</sup>

The mechanism of the effect of alloying Cu on the resistance to general corrosion of stainless steels was already studied.<sup>2),4),13),14)</sup> It was reported in the studies that deposited Cu on a corroded surface of the steels suppressed the anodic dissolution of the steels. However, the mechanism for localized corrosion in chloride media has not been clarified. The deposition of Cu on a locally corroded surface was recognized for both ferritic and austenitic stainless steels.<sup>7),15)</sup> However, its effect on localized corrosion resistance was different between

ferritic and austenitic stainless steels. Since Cu makes complex ions,<sup>16)</sup> such as  $\text{CuCl}_2^-$ , in chloride media, the stability of the deposited Cu should be reconsidered.

The purpose of the present study was to explain the effect of alloying Cu on the corrosion resistance in chloride media for both ferritic and austenitic stainless steels.

## 2. Experimental procedure

Chemical compositions of steels used are given in Table 1. Ferritic stainless steels were niobium (Nb)-bearing 22% chromium (Cr) steels and austenitic stainless steels were basically type 304 steels. Both ferritic and austenitic steels had two kinds of steels containing 0% Cu and 0.5% Cu. These steels were produced from 30 kg vacuum-melted ingots and hot rolled to 5 mm thick sheets and then cold rolled to 2 mm thick sheets with intermediate annealing and pickling. The conditions of the final annealing were 950°C-1 min for ferritic steels and 1100°C-1 min for

**Table 1. Chemical composition of steels used (mass%)**

No.	C	Si	Mn	P	S	Cr	Ni	Cu	Nb	N
F1	0.033	0.34	0.16	0.026	0.005	22.6	0.20	-	0.55	0.014
F2	0.031	0.31	0.15	0.028	0.006	22.2	0.21	0.55	0.53	0.014
A1	0.056	0.51	0.98	0.030	0.005	17.9	8.42	-	-	0.039
A2	0.055	0.52	0.99	0.031	0.005	18.1	8.51	0.51	-	0.047

austenitic steels.

Specimens for immersion tests were 30 x 30 x 2 mm pieces polished to #320 finish and degreased with acetone. Corrosion rates in 0.1 M H<sub>2</sub>SO<sub>4</sub> solutions at 80°C, 0.37 M FeCl<sub>3</sub> + 0.05 N HCl solutions at 35°C, and 1.2 M NaCl + 0.3 M H<sub>2</sub>O<sub>2</sub> solutions at 80°C were measured after 24 h immersion. Corrosion products in acid chloride media (0.2 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M NaCl) were analyzed by EPMA (JEOL, JSM-35CF).

Anodic polarization curves in deaerated 0.2-2 M H<sub>2</sub>SO<sub>4</sub> + 0-0.5 M NaCl solutions at 30°C were measured using a potentiostat. After 10 min-cathodic reduction at -0.45 V<sub>NHE</sub>, specimens were polarized in an anodic direction at the rate of 20 mV/min. These specimens were polished to #600 finish and sealed by silicon sealant except 10 x 10 mm measuring area. In order to estimate the dissolution potential in the stationary solution, the dissolution potential of pure metal Cu (99.99%) in acid chloride media (0-5 M Cl<sup>-</sup> + H<sub>2</sub>SO<sub>4</sub>; pH 1) at 25°C was measured by the anodic polarization method using a rotating disk electrode. The dissolution potentials at each rotating rate were determined as the potential at which the polarizing current became positive and the dissolution potential at 0 rpm was extrapolated from the potentials at 300-3000 rpm. In order to measure the potential at the bottom of a pit, an artificial pit was designed and the potentials inside and outside the pit were monitored. The details of the instrument are mentioned later. Pitting potentials were measured by the anodic polarization method without the cathodic treatment in deaerated 0.05-3 M NaCl solutions. Pitting potentials were determined as the most noble potential at which the anodic current was over 10 μA.

### 3. Results

#### 3.1 Effect of Cu on the resistance to general corrosion and localized corrosion

Results of immersion test in sulfuric acid solutions and chloride media are shown in Fig. 1. In agreement with previous works,<sup>1)-5)</sup> the addition of Cu decreased the corrosion rate in sulfuric acid solutions (0.1 M H<sub>2</sub>SO<sub>4</sub>) for both ferritic and austenitic stainless steels. In the case of ferric chloride solutions (0.37 M FeCl<sub>3</sub> + 0.05 N HCl), the addition of Cu was beneficial for ferritic stainless steels, but harmful for austenitic steels. In this case, the addition of Cu showed different effects between ferritic and austenitic steels. From the viewpoint of anodic reactions, the mechanism of the improvement of corrosion resistance by addition of Cu is considered that dissolved Cu forms metal deposits on a corroded site and the deposited Cu suppresses an anodic dissolution.<sup>2),4),13),14),17)</sup>

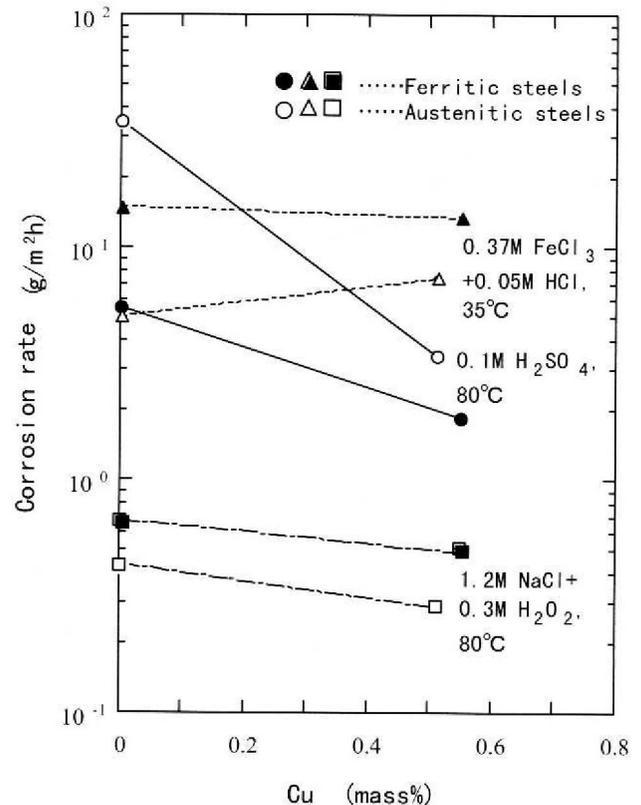


Fig. 1. Effect of Cu on the corrosion resistance of ferritic and austenitic stainless steels in various solutions.

However, the deposited Cu may not be stable even at a corroded anode site in ferric chloride solutions because the reduction current density of ferric chloride is large and its redox potential is considerably noble. Redox potential of  $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$  reaction is 0.771 V<sub>NHE</sub> and the open circuit potential of a platinum (Pt) electrode in the ferric chloride solution was 0.983 V<sub>NHE</sub> at 35°C. This potential is much nobler than the redox potentials of  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$  (0.337 V<sub>NHE</sub>) and  $\text{CuCl}_2 + \text{e}^- \rightarrow \text{Cu} + 2\text{Cl}^-$  (0.208 V<sub>NHE</sub>).

The pitting corrosion resistance of the steels was investigated in 1.2 M NaCl + 0.3 M H<sub>2</sub>O<sub>2</sub> solutions which contained the same concentration of Cl<sup>-</sup> as 0.37 M FeCl<sub>3</sub> + 0.05 N HCl solutions but the reduction current density of hydrogen peroxide was smaller. The open circuit potential of a Pt electrode in this solution was 0.600 V<sub>NHE</sub> at 80°C. In this solution, the addition of Cu was beneficial for both ferritic and austenitic stainless steels, as shown in Fig. 1. Alloying Cu had a beneficial effect in the condition that the specimens corroded at relatively active potential.

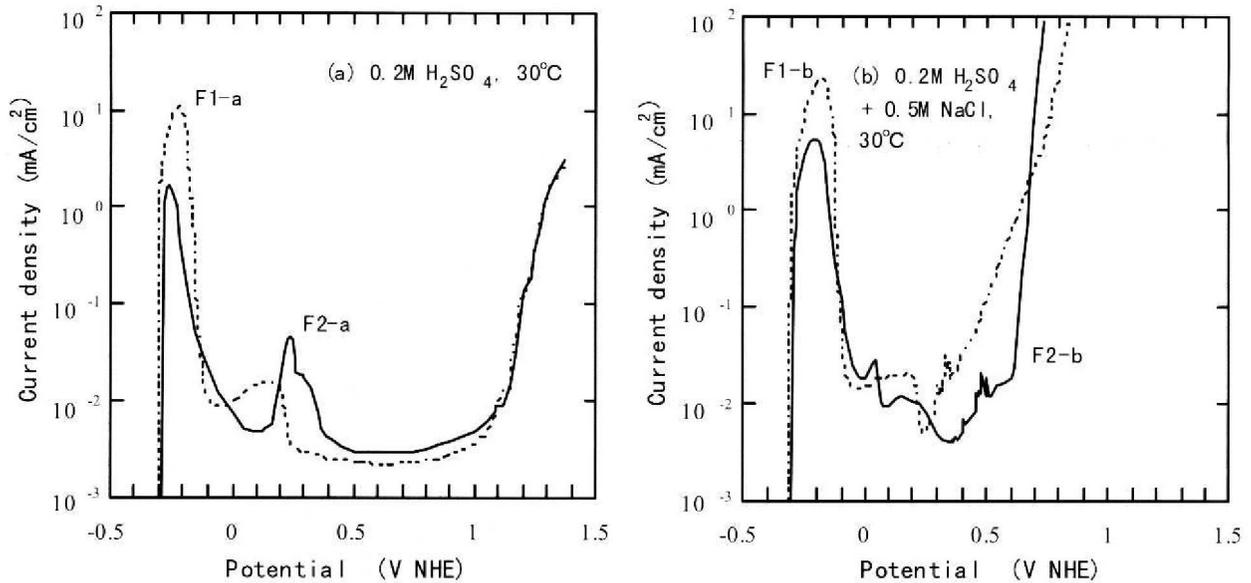


Fig. 2. Effect of Cu on anodic polarization curves for ferritic stainless steels in 0.2 M H<sub>2</sub>SO<sub>4</sub> solutions (F1-a, F2-a) and 0.2 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M NaCl solutions (F1-b, F2-b).

### 3.2 Effect of Cu on anodic polarization behavior

Anodic polarization curves were measured in order to investigate the deposition and dissolution behavior of alloying Cu in sulfuric acid solutions and acid chloride media. The results for ferritic stainless steels are shown in Fig. 2. The peak current density was suppressed by the addition of Cu. A small second peak on the anodic polarization curve of the Cu-bearing stainless steel in the sulfuric acid solution was detected at 0.25 V<sub>NHE</sub>. This small peak corresponds to the dissolution of Cu that then redeposited elsewhere on the specimen surface during the active dissolution, as reported by Guo et al.<sup>17)</sup> In the solution containing 0.5 M NaCl, the peak current density was also suppressed by the addition of Cu. The small second peak corresponding to the dissolution of deposited Cu shifted in an active direction by about 0.2 V with the addition of 0.5 M NaCl to the solution. This result means that Cl<sup>-</sup> decreases the stability of deposited Cu.

Judging from the height of small second peaks, the deposition of Cu in the acid chloride media was estimated to be smaller than that in the sulfuric acid solutions.

The same anodic polarization behavior as the ferritic stainless steels was observed for the austenitic stainless steels.

### 3.3 Morphology of deposited Cu

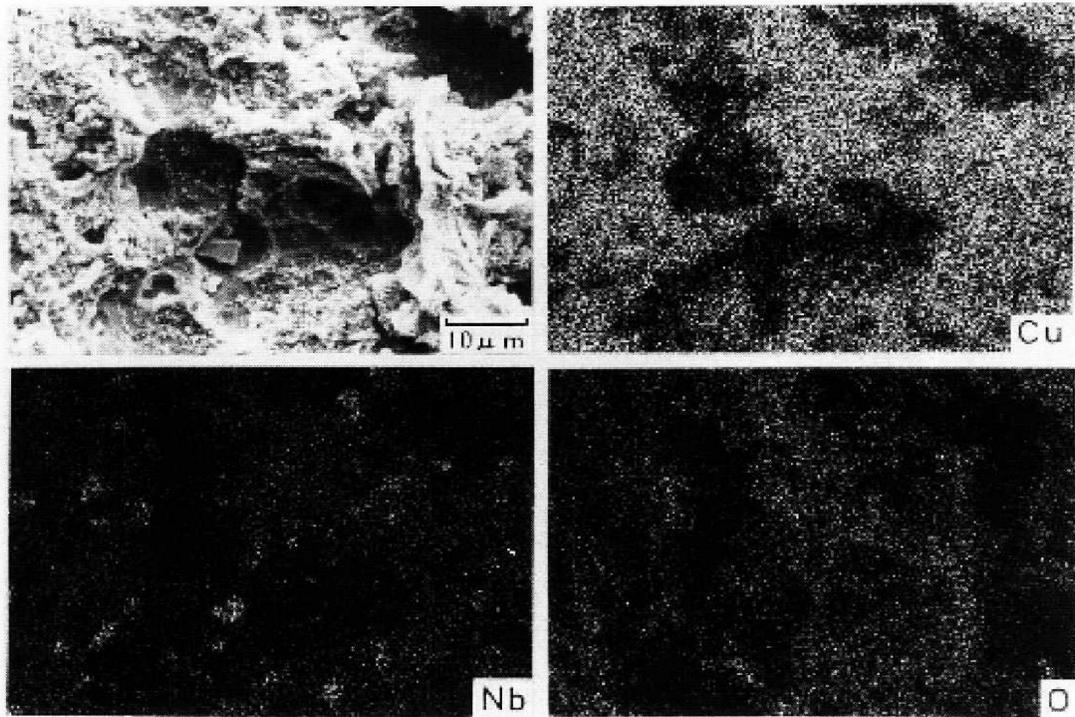
Figs. 3(a) and 3(b) are the secondary electron images of corrosion products on the specimens which had been exposed to acid chloride media (0.2 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M

NaCl). In the case of the Cu-bearing ferritic stainless steel, powdery corrosion products covered the surface of the steel uniformly. The product consisted of metallic Cu mainly and contained Nb, Ni, and their oxides slightly. It was reported that CuCl was easily produced in low pH chloride media.<sup>18)</sup> However, CuCl was not produced in this environment because Cl<sup>-</sup> was not detected in the corrosion products and the corrosion potential was more active than the redox potential of  $\text{CuCl} + \text{e}^- \rightarrow \text{Cu} + \text{Cl}^-$  (0.137 V<sub>NHE</sub>). In the case of the Cu-bearing austenitic stainless steel, granular corrosion products were deposited nonuniformly on the surface of the steel. EPMA analysis showed the corrosion products were almost pure metallic Cu for both ferritic and austenitic Cu-bearing stainless steels.

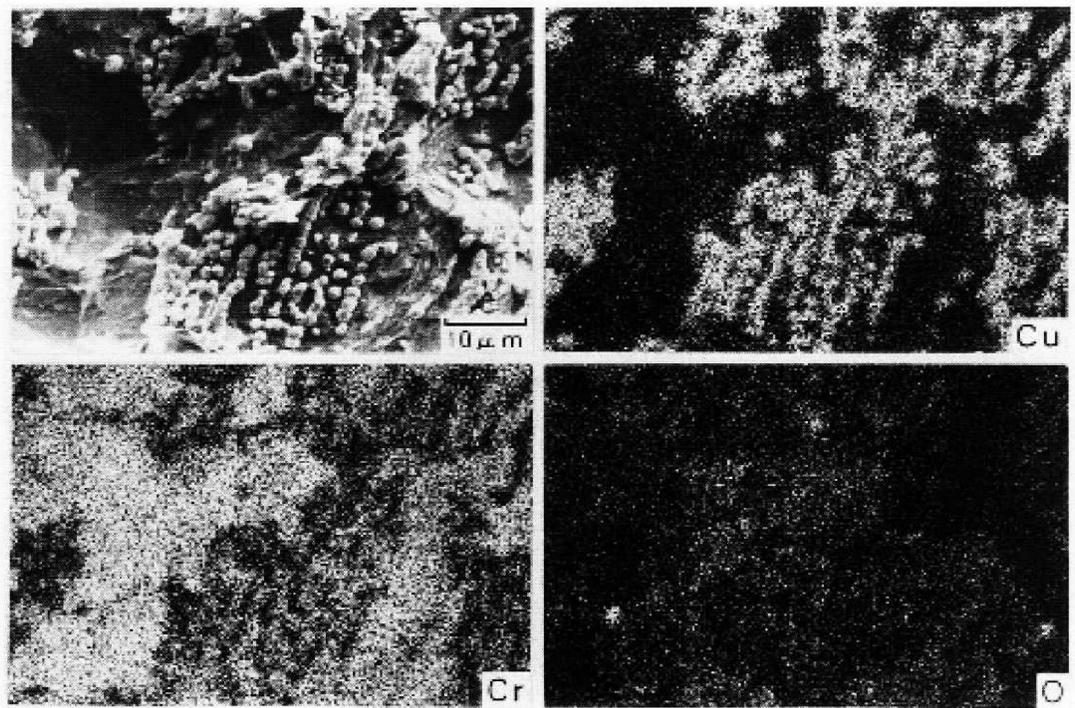
Judging from the morphology of the deposited Cu, the suppression of anodic dissolution by the deposited Cu is more effective for the ferritic stainless steel than for the austenitic steel because the Cu particles are in more intimate contact with the surface in the former case.

### 3.4 Dissolution potential of Cu

The anodic polarization curves in Fig. 2 showed that the dissolution potentials of the deposited Cu in the acid solutions shifted in an active direction by the addition of Cl<sup>-</sup>. The effects of Cl<sup>-</sup> and Cu<sup>2+</sup> on the dissolution potential of pure metal Cu was investigated to clarify the stability of deposited Cu. Fig. 4 shows the dissolution potential of the copper. The dissolution potential of Cu dropped

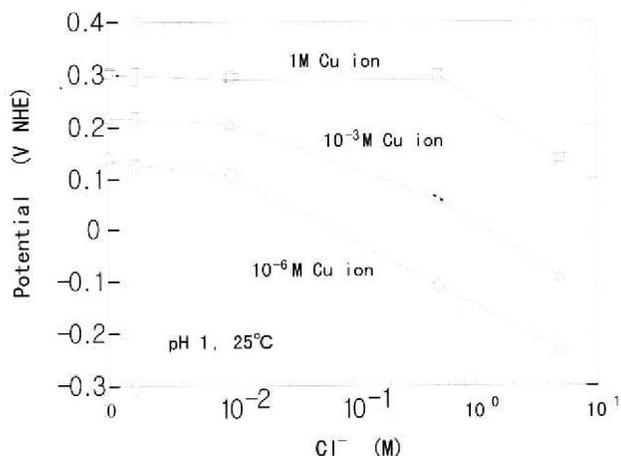


(a) F2 (ferritic stainless steel containing 0.5% Cu)



(b) A2 (austenitic stainless steel containing 0.5% Cu)

**Fig. 3.** Characteristic X-ray images of the surfaces of (a) F2 steel and (b) A2 steel immersed in 0.2 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M NaCl solutions for 24 h at 50°C and 80°C, respectively.



**Fig. 4.** Effects of  $\text{Cl}^-$  and Cu ions on the dissolution potential of copper in sulfuric acid solutions (pH 1) at  $25^\circ\text{C}$ .  $\text{Cl}^-$  and Cu ions were added by NaCl and  $\text{CuSO}_4$ , respectively.

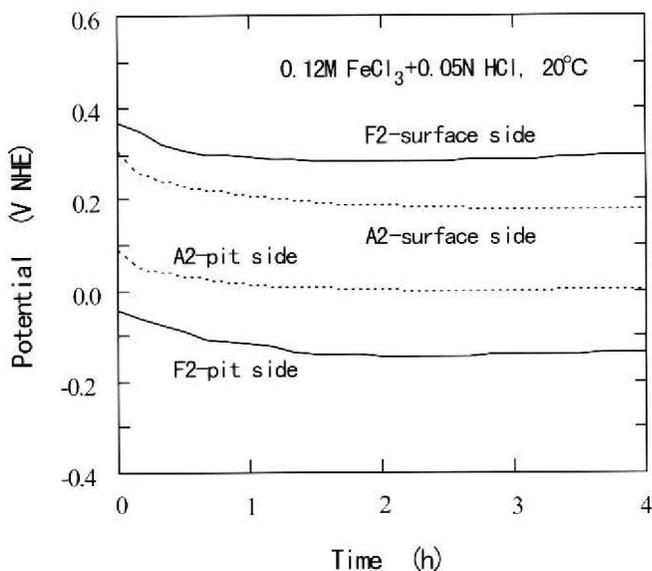
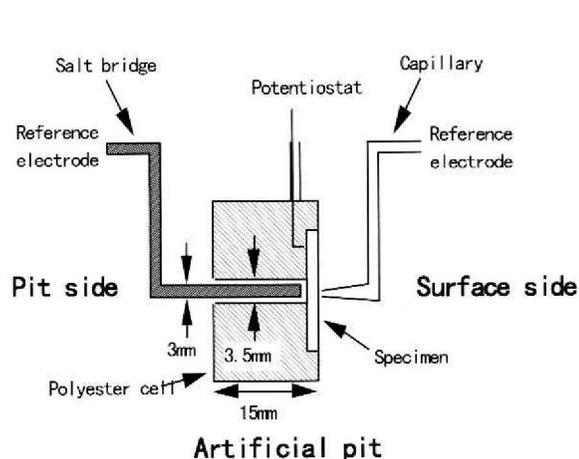
considerably in an active direction with the increase of  $\text{Cl}^-$  concentration, because copper dissolves as  $\text{CuCl}_2^-$  or  $\text{CuCl}_3^{2-}$  in acid chloride media.<sup>19-21)</sup>

Since the  $\text{Cl}^-$  concentration of the solution inside an active pitting and crevice corrosion site is much more than 0.5 M, the dissolution potential of Cu in the site must be even more negative. If the inside solution of the pits contains 5 M  $\text{Cl}^-$ , the dissolution potential of Cu drops to  $-0.09 V_{\text{NHE}}$  in the solution containing  $10^{-3} \text{ M Cu}^{2+}$ .

### 3.5 Corrosion potential of locally corroded site

Since the stability of deposited Cu decreases in chloride media, the corrosion potential of locally corroded sites is

important for the suppression of anodic dissolution by the deposited Cu. As the potential inside a pit is considered to be more active than that outside a pit, the corrosion potentials inside and outside an artificial pit in a ferric chloride solution were investigated. The artificial pit is shown in Fig. 5. A specimen with a lead wire was filled in a polyester resin that has a thickness of 15 mm and 25 mm in diameter. A hole with 3.5 mm in diameter was drilled on the back side for an artificial pit and the front side was for a cathodic area. The potential inside the pit was measured through a salt bridge with 3.0 mm in diameter. 0.12 M  $\text{FeCl}_3 + 0.05 \text{ N HCl}$  solution ( $20^\circ\text{C}$ ) was adopted in order to avoid the occurrence of pitting corrosion on the front cathodic surface. The open circuit potential of a Pt electrode in the solution was  $0.921 V_{\text{NHE}}$  which was close to that in 0.37 M  $\text{FeCl}_3 + 0.05 \text{ N HCl}$  solution ( $35^\circ\text{C}$ ). Since the structural restriction against solution convection in the artificial pit was not so severe as normal crevices such as washers, the pit did not corrode at the beginning of the experiment. Electrolysis at the condition of 2 mA anodic current for 2 h with sealing of the front cathodic surface was carried out to initiate the corrosion inside the pit. After the electrolysis, the seal on the front cathodic surface was removed and the change in potentials of the pit and the cathodic area was monitored. The potential at the bottom of the pit for the Cu-bearing ferritic stainless steel was about  $-0.14 V_{\text{NHE}}$  and that for the Cu-bearing austenitic steel was about  $0 V_{\text{NHE}}$ . The difference of the potentials between ferritic and austenitic steels affects the stability of the deposited Cu



**Fig. 5.** Corrosion potentials of a surface side and a pit side of the artificial pit specimens.

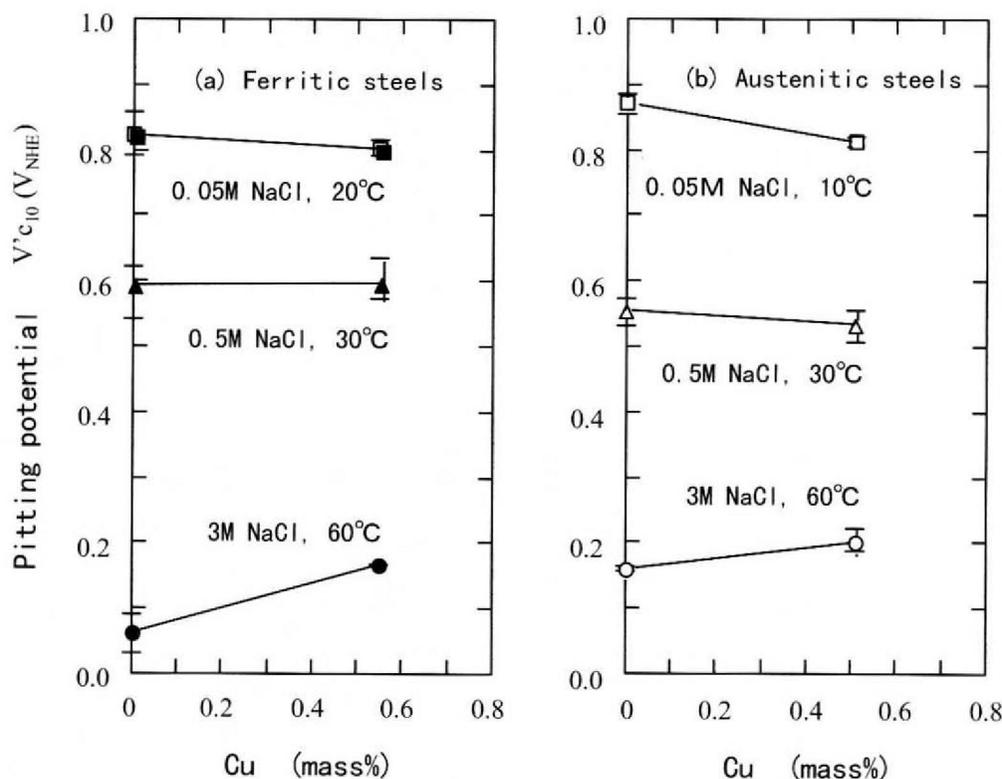


Fig. 6. Effect of Cu on the pitting potentials of ferritic and austenitic stainless steels in various chloride media.

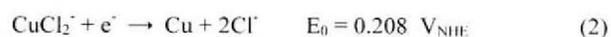
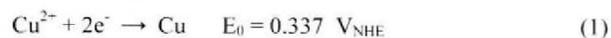
inside a pit. The ferritic steel has advantages for the stability of the deposited Cu.

### 3.6 Effect of Cu on pitting potential

Usually it has been said that the addition of Cu is beneficial for the pitting potential of ferritic stainless steels but harmful for that of austenitic steels. In order to examine this conventional understanding, pitting potential was measured in various chloride media. Results are shown in Fig. 6. Even in the austenitic stainless steels, addition of Cu had a beneficial effect when a pitting occurred in enough active potential range. On the contrary, it had a harmful effect even in the ferritic stainless steels when a pitting occurred in enough noble potential range. We<sup>22,23)</sup> and other researchers<sup>10,24)</sup> already reported that the effect of alloying Cu on pitting and crevice corrosion potential changed with potential range. The turning point in the potential at which the effect of alloying Cu changed from beneficial to harmful in ferritic stainless steels was more noble than that in austenitic steels. That difference is considered to be ascribed to the difference of the corrosion potential inside a pit between ferritic and austenitic stainless steels.

## 4. Discussion

In the case of localized corrosion in neutral chloride media, anodic reactions occur inside a pit or crevice, in which the pH of the solution is low and the  $\text{Cl}^-$  concentration is high. The corrosion potential of steels is relatively active. Cu dissolves as  $\text{Cu}^{2+}$  in low pH and  $\text{Cl}^-$ -less solutions.<sup>17,25)</sup> According to the potential-pH-Cl diagram of Cu,<sup>21)</sup> Cu dissolves as  $\text{CuCl}_2^-$  in low pH solutions containing  $\text{Cl}^-$ . When Cu dissolves as ionic species, the reactions are as follows.



Besides, there is the equilibrium between  $\text{Cu}^{2+}$  and  $\text{CuCl}_2^-$ .



When the equilibrium (3) is maintained at each dissolution potential of Cu in Fig. 4, the concentration of  $\text{Cu}^{2+}$  and  $\text{CuCl}_2^-$  can be calculated from the Nernst equation of the equilibrium (3) in the case that the total concentration of

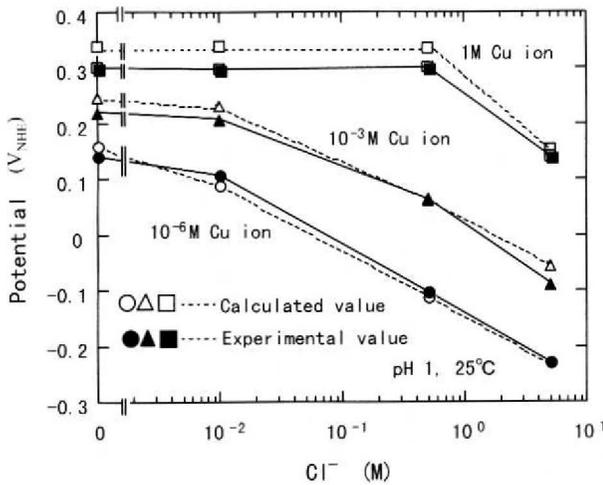


Fig. 7. Dissolution potential of Cu in sulfuric acid solutions containing Cl<sup>-</sup> and Cu ions derived from Fig. 4 and calculated from Table 2.

Cu ions equals 1, 10<sup>-3</sup> and 10<sup>-6</sup> M and the concentration of Cl<sup>-</sup> equals 0, 10<sup>-2</sup>, 0.5 and 5M. The calculated results are shown in Table 2. Cu dissolves as CuCl<sub>2</sub><sup>-</sup>, when the concentration of Cl<sup>-</sup> is more than 0.5 M and total Cu ion concentration is less than 1 M. Since the concentration of Cl<sup>-</sup> inside a pit or crevice is usually more than 0.5 M, Cu dissolves as CuCl<sub>2</sub><sup>-</sup>. Based on the concentrations of Cu<sup>2+</sup> and CuCl<sub>2</sub><sup>-</sup> in Table 2, the equilibrium potentials of Eqs. (1) and (2) are calculated by the Nernst equations. Cu dissolves at more active potential in the equilibrium potentials of Eq. (1) or Eq. (2). Fig. 7 shows the calculated dissolution potentials and the experimental ones derived from Fig. 4. Both data show good agreement, which indicates the validity of the results in Table 2.

Cu dissolves as CuCl<sub>2</sub><sup>-</sup> in a locally corroded site. Depending on the potential inside a pit or crevice, Cu deposits as metallic Cu or dissolves as CuCl<sub>2</sub><sup>-</sup>. When Cu deposits, it forms a protective film. Undeposited Cu ion flows out of a pit or crevice.

In the case of general corrosion, the corrosion potential

of Cu-bearing stainless steels is usually active and deposited Cu is stable. The deposited Cu suppresses the anodic dissolution of the steels (Fig. 2(a)). The suppressing effect of the deposited Cu is effective even in the solutions containing Cl<sup>-</sup> (Fig. 2(b)). However, Cl<sup>-</sup> diminishes the stability of the deposited Cu (Fig. 4). The condition of the inside solution of localized corrosion such as pitting and crevice corrosion is low pH and high Cl<sup>-</sup> concentration. Therefore, the stability of the deposited Cu affects the effectiveness of alloying Cu on the resistance to localized corrosion. Alloying Cu has beneficial effects when the steels corrode at active potential, but does not have beneficial effect at noble potential (Fig. 6).

The reason that alloying Cu has a beneficial effect in ferritic stainless steels more than in austenitic stainless steels is because the more active corrosion potential of ferritic steels than that of austenitic steels makes the deposition of Cu easy; and further that the deposited Cu covers the anodic surface much more uniformly.

According to our data, alloying Cu shows a harmful effect in the noble potential range. We investigated the harmful effect of alloying Cu and found that the passive film of Cu-bearing stainless steels was destroyed by Cl<sup>-</sup> attack more easily than that of Cu-less steels.<sup>26)</sup> It was suggested that the dissolution of Cu complex ions such as CuCl<sup>+</sup>, CuCl<sub>4</sub><sup>2-</sup>, CuCl<sub>2</sub><sup>-</sup> and CuCl<sub>3</sub><sup>2-</sup> might assist the destruction of the passive films. However, the detail of the harmful effect of alloying Cu is still unknown.

### 5. Conclusions

In order to explain the effect of alloying Cu on the corrosion resistance of stainless steels in chloride media for both ferritic and austenitic stainless steels, the corrosion behavior of Cu-bearing stainless steels was investigated. Conclusions are as follows.

- (1) Alloying Cu redeposited on the anodic surface of the steels during active dissolution and improved the corrosion resistance through the suppression of the active

Table 2. Concentration of Cu<sup>2+</sup> and CuCl<sub>2</sub><sup>-</sup> calculated from the dissolution potentials of Cu in Fig. 4.

Total Cl <sup>-</sup> concentration	Cu ion concentration					
	Total 10 <sup>-6</sup> M		Total 10 <sup>-3</sup> M		Total 1 M	
	Cu <sup>2+</sup>	CuCl <sub>2</sub> <sup>-</sup>	Cu <sup>2+</sup>	CuCl <sub>2</sub> <sup>-</sup>	Cu <sup>2+</sup>	CuCl <sub>2</sub> <sup>-</sup>
0 M Cl <sup>-</sup>	10 <sup>-6</sup> M	0 M	10 <sup>-3</sup> M	0 M	1 M	0 M
0.01 M Cl <sup>-</sup>	0.008 M	0.992 × 10 <sup>-6</sup> M	0.370 × 10 <sup>-3</sup> M	0.630 × 10 <sup>-3</sup> M	0.996 M	0.381 × 10 <sup>-2</sup> M
0.5 M Cl <sup>-</sup>	0 M	10 <sup>-6</sup> M	0 M	10 <sup>-3</sup> M	0.762 M	0.238 M
5M Cl <sup>-</sup>	0 M	10 <sup>-6</sup> M	0 M	10 <sup>-3</sup> M	0 M	1 M

dissolution even in acid chloride media.

(2) The dissolution potential of the deposited Cu shifted in an active direction with the increase of Cl<sup>-</sup> concentration. The suppression of anodic reactions by the deposited Cu was useful only in its stable potential range. Deposited Cu dissolved as CuCl<sub>2</sub><sup>-</sup> in solutions of low pH and high Cl<sup>-</sup> concentrations above the stable potential range.

(3) The reason that alloying Cu has a beneficial effect in ferritic stainless steels more than in austenitic steels is because the more active corrosion potential of ferritic steels than that of austenitic steels makes the deposition of Cu easy; and further that the deposited Cu covers the anodic surface much more uniformly.

(4) Alloying Cu has the harmful effect on the localized corrosion resistance in the noble potential range for both ferritic and austenitic stainless steels. The resultant effect of alloying Cu on the localized corrosion resistance depends on the competitive relationship between the beneficial effect and the harmful effect.

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