

The Pitting Inhibition of Fe-Cu Alloy in Weakly Alkaline Solution under Wet-Dry Condition

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(Received May 2, 2007 : Accepted June 10, 2007)

Abstract : Pure iron, Fe-0.4, and 1.2 wt.%Cu alloys were examined by conducting the electrochemical techniques in the weakly alkaline solution, pH9, controlled by Ca(OH)₂ solution added with 0.02M NaCl. The R_p measured from ac impedance, selected 10 kHz and 10mHz, in weakly alkaline solutions containing chloride ions indicated that the addition of copper up to 1.2wt.% into the pure iron significantly improved the pitting resistance of iron. In contrast to alloy, the pure iron showed the rapid pitting occurrences in drying period. During the drying period, the corrosion potential of pure iron was shifted to less noble value, pitting initiation.

Keywords : Alloy, Pitting, AC impedance, Atmospheric.

1. Introduction

The application of electrochemical techniques to the corrosion monitoring in atmospheric circumstance is quite difficult because atmospheric corrosion proceeds under thin electrolyte layers. The main limitation was IR drop on surface and the inapplicability of the conventional electrochemical set-up employing a Luggin probe to atmospheric corrosion studies owing to the presence of thin electrolyte layers over specimen, leading to serious errors in the measurement of the atmospheric corrosion rate.^{2,5)} However, Nishikata^{1,2,5)} et al. introduced a settlement in this area when they employed the ac impedance technique to monitor the corrosion rates of carbon steel, copper and weathering steels exposed to wet-dry cycles. Through the measurements of ac impedance, the solution resistance is estimated from impedance measured in high frequency range, while the sum of the polarization resistance and the solution resistance is estimated from the impedance in the low frequency range. It is well known that the polarization resistance is inversely proportional to corrosion rate in aqueous solution. Thus, this technique has been reported to be very useful for monitoring the atmospheric corrosion rates in atmospheric corrosion system.

On the other hand, the corrosion rates of iron in concrete are very slow and fully passivated without the chloride ion and concrete neutralization. In the media containing chloride, the corrosion rate is increased by breakdown of passive film and the localized attack is observed. Pitting attack of iron has been studied extensively to now, especially in acidic and

neutral chloride solutions.³⁾

In this study, the effects of copper on the pitting inhibition of steel under wet-dry condition with weakly alkaline solution were investigated in order to propose the application of scraps containing a high copper concentration as material of reinforcing steels in concrete structures.

2. Experimental Methods

2.1 Cell for ac impedance measurement⁷⁾

3-electrodes cell arrangement was used in this study, as shown in Fig. 1. The specimen with same dimensions, 1 cm², were embedded about 0.2 mm apart in parallel and epoxy resin. A barrier wall with 0.5 mm height was then set around the electrode. The capillary tip hole was made inside resin to measure the corrosion potential E_{corr} with a conventional Luggin capillary. The test electrode material were pure iron and Fe-Cu alloys (copper contents 0.4 and 1.2 wt.%).

2.2 Wet-Drying Cycles⁷⁾

The electrochemical measurements of specimen were monitored by the ac impedance method under a cyclic wet-dry condition for 24 hours, which was conducted by exposure to alternate conditions of 1h immersion in a simulated pH9 concrete solution by (Ca(OH)₂) containing 0.02 M NaCl and 3 hour-drying at 298 K and 50%RH.

The measurement of impedance at 10 kHz (Z_H) and 10 mHz (Z_L) with 10 mV amplitude was conducted continuously using an FRA (S-5720C, NF Circuit Block Co. Japan) by combining the potentiogalvanostat (HA-303, Hokudo Denko Co., Japan) controlled by a computer through the GPIB interface.

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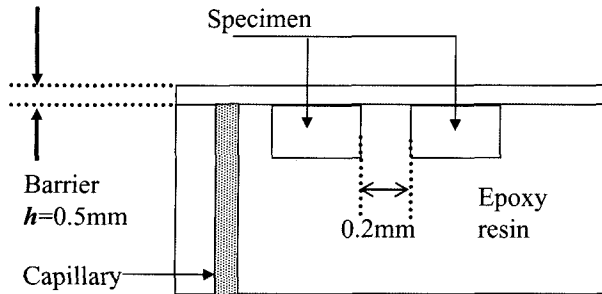


Fig. 1. Experimental cell used for the ac impedance measurement for monitoring of pitting occurrences under wet-drying condition.

2.3 Potentiodynamic and galvanostatic polarization³⁾

The corrosion behaviors of iron and Fe-Cu alloys were examined by conducting potentiodynamic polarization with 1mV/sec scan rate in $\text{Ca}(\text{OH})_2$ solution with 0.02MNaCl. The galvanostatic measurements of pure copper were polarized with $\pm 25 \mu\text{A}/\text{cm}^2$ in pH9 solution. The solution of both measurements were deaerated with N_2 gas for 24hours. An Ag/AgCl/saturated KCl reference was used for above measurements.

3. Results and Discussions

3.1 Pitting occurrences in wet-dry condition

3.1.1 Pure iron

The corrosion rates of the pure iron as shown in Fig. 2 were greatly accelerated by the wet-dry cycles, in contrast to alloys. The surface of pure iron was covered with corrosion products and observed with many pit holes. The pit holes shown with Fig. 3, having the depth of 30 to 80 μm , were also confirmed with laser microscope. But, in case of alloys the pit holes were not formed on the surface. From the second wet-dry cycle, the pitting rates of pure iron showed the drastic increases during the drying periods. As the thickness of the electrolyte layer on surface is decreased, oxygen is reduced with more rapid rates and chloride concentration accumulated, leading to much higher pitting occurrences than wetting condition.^{3,7)}

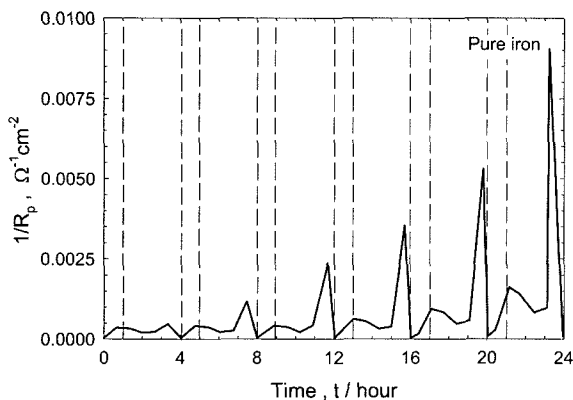


Fig. 2. The monitoring result of pure iron in pH9 solution containing with 0.02MNaCl under wet-drying condition for 24 hours.

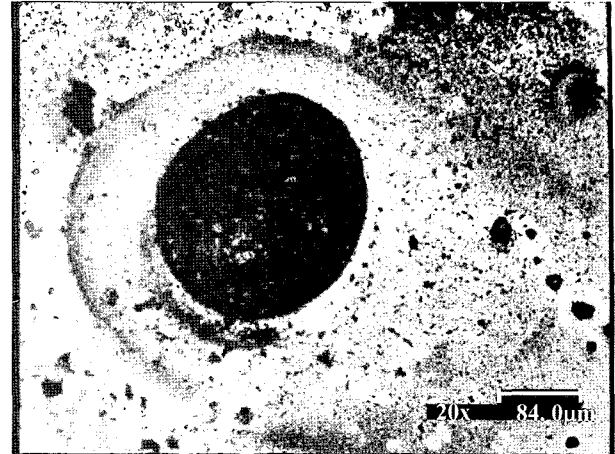


Fig. 3. The pitting holes on pure iron surface observed with laser microscope after wet-drying condition.

3.1.2 Fe-0.4 and 1.2 wt.%Cu

Fe-Cu alloys in Fig. 4(a), (b) showed that their corrosion rates were very small if the surface showed with a visibly thick electrolyte layer and even at the drying condition, the corrosion rate did not show a pronounced maximum. In Fig. 5, the changes of corrosion potentials for pure iron and Fe-1.2 wt.%Cu in the 5th and 6th cycles are shown. In potential monitoring, the capillary was in contact with the cell through the salt bridge in epoxy resin. The corrosion potentials for both specimens were shifted rapidly to noble values owing to drying up of the wetness between the specimen and capil-

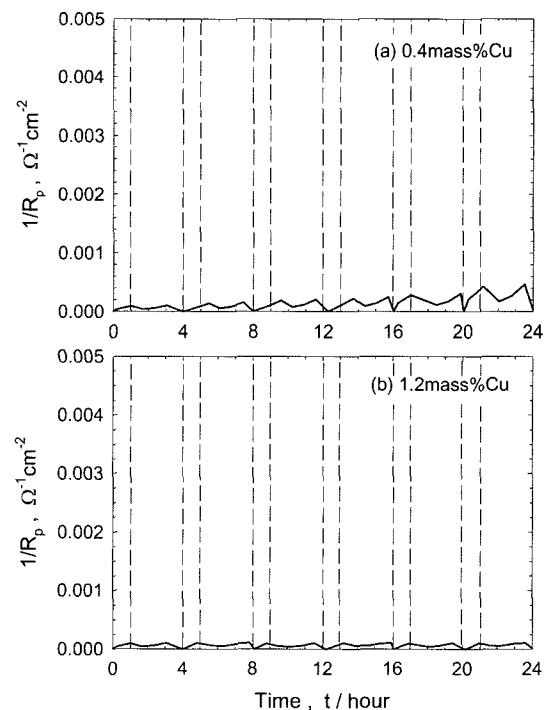


Fig. 4(a), (b) The monitoring result of 0.4mass% Cu and 1.2mass%Cu in pH9 solution containing with 0.02MNaCl under wet-drying condition for 24 hours.

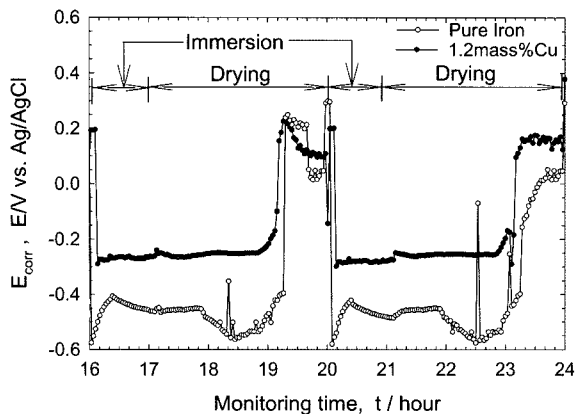


Fig. 5. The variation of corrosion potentials of pure iron and 1.2 mass%Cu in pH9 solution containing with 0.02 MNaCl under wet-drying condition.

lary, approximately 2 hours later when the drying process was begun. Namely, those data showed the uncertain E_{corr} measurements. However, the pitting occurrences on drying process showed the different patterns according to pure iron and alloys. The potential changes of pure iron showed the less noble shift, from -0.45 V to -0.60 V, of pitting initiation afterwards 1 hour later in drying process. This behavior is very similar to that observed by R. P. Vera Cruz^{2,5)} in their different types of stainless steel exposed to thin NaCl electrolyte layer. In contrast to the pure iron, the potential changes of 1.2 wt.%Cu showed a stable and high tendency in the drying process before the drying up of wetness between the specimen and capillary. This specimen shows good corrosion resistance and remained passive throughout the exposure. The initially high corrosion rate can be attributed to a lack of a competent passive film initially, since the 1.2 wt.%Cu was subjected to surface polishing prior to the start of exposure. However, the passivation takes place immediately as a competent passive film is produced, as reflected in the lower values of the corrosion rate.^{3,7,9)} On the other hand, the corrosion potential of iron in wetting condition was changed from less noble potential to more noble value, showing with reduction of corrosion products in pit holes. This appearance was not showed with alloy.

3.2 Potentiodynamic and galvanostatic measurements

Fig. 6 shows the anodic polarization curves for pure iron and Fe-1.2 wt.%Cu in pH9 solution added with 0.02M NaCl. The anodic current of Fe-Cu alloys decreased very much. The corrosion potential of alloy was measured at -0.36 V (vs. Ag/AgCl), more positive 0.25 V than pure iron. The anodic polarization curve of Fe-1.2 wt.%Cu showed the low current density, less than 10 mAcm^{-2} , to -0.15 V. However, pure iron showed the pitting occurrences at the potential range. The corrosion potential of 1.2 wt.%Cu in Fig. 6 was shifted closely to the side of pure copper, leading to the Cu_2O formation on alloy surface.

The anodic behavior of 1.2 wt.%Cu, as shown below, indicates the $\text{Cu}_2\text{O}/\text{Cu}$ reaction together with Fe/Fe^{2+} reaction on the

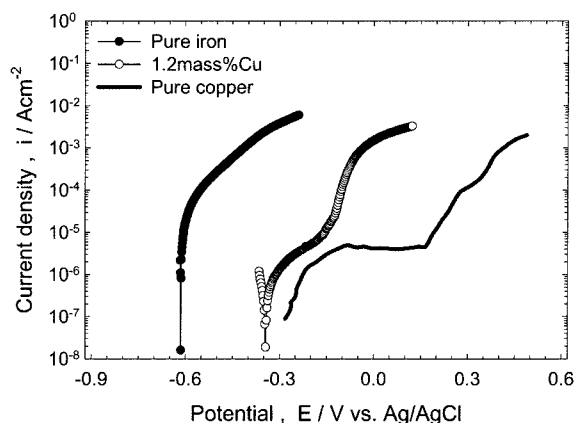


Fig. 6. The anodic polarization curves with 1mV/Sec in pH9 solution containing with 0.02MNaCl under aqueous condition.

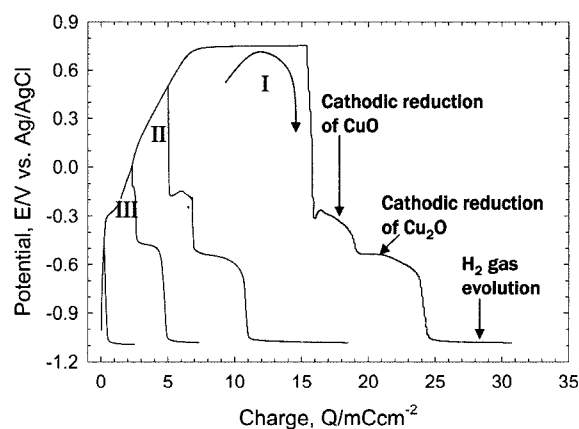
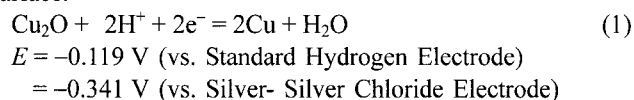


Fig. 7. The anodic and cathodic galvanostatic polarization curves with $\pm 25 \mu\text{Acm}^{-2}$ in pH9 solution.

surface.⁶⁾



It is considered that the transitions of corrosion potential of alloys were attributed to the preferential dissolution of the less noble metal of the alloy with the more noble metal accumulated on the alloy surface.^{3,7)}

Fig. 7 shows that the galvanostatic measurement of pure copper were conducted in same pH9 solution. The measurement was done with $\pm 25 \mu\text{A}/\text{cm}^2$. The cathodic polarization of scan I showed the potential pauses on the reduction of CuO and Cu_2O oxide, and H_2 gas evolution. Therefore, the scan III of cathodic polarization is corresponded with the reduction of copper oxide, Cu_2O reduction, which the 1.2 wt.%Cu was polarized in the range of -0.35 V to -0.15 V in Fig. 7, the passivated region. The potential pause of the cathodic reduction of CuO oxides were appeared clearly together with the potential pause of Cu_2O reduction at the moment when the pure copper was polarized over $+0.4$ V.³⁾ It is considered that the pitting resistance of alloy was attrib-

uted to Cu_2O film on the surface from the results of the potential changes, from -0.3 V to $+0.2\text{ V}$, of 1.2 wt.%Cu during the drying condition, although it was impossible to measure the potential measurement due to the drying up between the specimen and capillary, and the results of Fig. 5 was conducted in wet and drying environment, aeration condition.^{3,8)}

4. Conclusions

From the experimental results of the effects of copper on the corrosion resistance of steel under wet-dry condition, it could be concluded as follows.

The pitting rates under a atmospheric condition were accelerated with the increase of chloride concentration owing to a decreasing water film thickness, leading to the shifts of less noble corrosion potential. Pure iron showed the extremely high pitting rates during the drying period, while the corrosion rates of alloy were drastically decreased to passivation. The corrosion potential changes of alloy showed the noble and stable values even during drying process.

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