Monitoring of Corrosion Rates of Fe-Cu Alloys under Wet-Dry Condition in Weakly Alkaline Environments

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When the steel, containing scrap elements like copper, is used as reinforcing steel bars for concrete, the steel is exposed to alkaline environments. In this study, AC impedance technique has been applied to the monitoring of corrosion rates of iron and several Fe-Cu (0.4,3,10wt%) alloys in a wet-dry cycle condition. The wet-dry cycle was conducted by exposure to alternate conditions of 1hour-immersion in a simulated pH10 concrete solution ($Ca(OH)_2$) containing 0.01M NaCl and 3hour-drying at 298K and 50%RH. The corrosion rate of the iron is greatly accelerated by the wet-dry cycles. Because the active FeOOH species, which are produced by the oxidation of Fe(II, III)oxide in air during drying, act as very strong oxidants to the corrosion in the wet condition. As the drying progresses, iron shows a large increase in the corrosion rate and a small shift of the corrosion potential to the positive values. This can be explained by acceleration of oxygen transport through the thin electrolyte layer. In contrast to iron, the Fe-Cu alloys show low corrosion rates and the high corrosion potentials in whole cycles.

Keywords : concrete, Fe-Cu alloys, corrosion monitoring, AC impedance, wet-dry cycles

1. Introduction

It has been shown previously[1] that the stage of drying is the most important during the atmospheric corrosion of iron and steel. Additionally, it is mentioned, that during this stage the alloying element Cu is able to retard the corrosion rate significantly. The reason may be either the surface can be passivated easily, e.g. by an enrichment of the element copper in the ferrous oxides or the oxygen reduction reaction is kinetically slow on the oxide scales formed on the Fe-Cu alloys. In both cases the rate of the metal dissolution will be slow during drying, yet the corrosion potentials will be positive if the surface is passivated, whereas they will stay rather negative if the kinetics of the oxygen reduction is slow.[2]

The application of electrochemical techniques to the corrosion monitoring in such a circumstance is quite difficult because atmospheric corrosion proceeds under extremely thin electrolyte layers. The largest problem in its application is that solution resistance becomes extremely high when the thickness of the electrolyte is very thin. In such case, an extremely high ohmic drop leads to serious errors in the measurement of the atmospheric corrosion rate. But, by 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 was reported to be very useful for monitoring the atmospheric corrosion rates in atmospheric corrosion system.[3],[4]

In this paper, the corrosion rates of steels with different copper contents (0,0.4,3,10wt%) were monitored by the AC impedance method under a cyclic wet-dry condition in a concentrated simulated concrete solution.

2. Experimental

A schematic diagram of the electrochemical cell used in impedance measurement is shown in Fig. 1. Two electrode cell arrangement was used in this study. A pair of specimen(10 mm X 2 mm) was embedded about 0.2mm apart in parallel, in epoxy resin. A barrier wall of 0.5mm height was then set around the electrode to ensure constancy of water layer thickness at each starting point of the dry period. The capillary tip hole was made inside
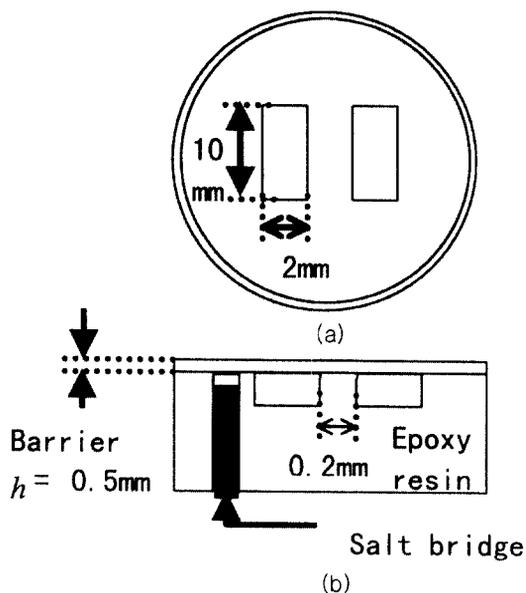
Fig. 1. Experimental cell used for the impedance measurement : (a) top view, (b) side view
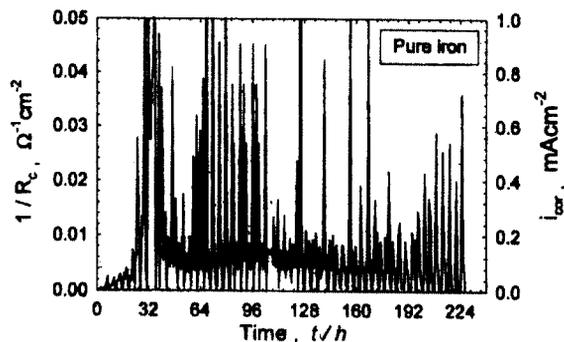

Fig. 2. Changes in corrosion rates of the pure iron during wet-dry cycles
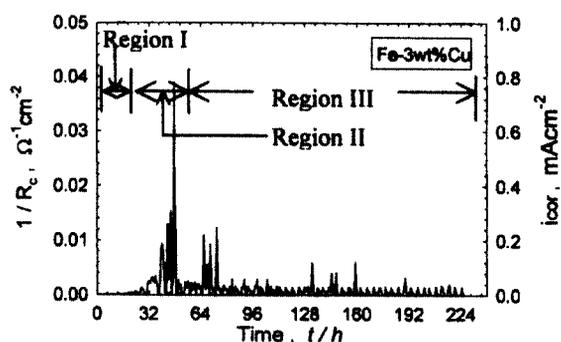
Fig. 3. Changes in the corrosion rates of Fe-3wt%Cu under a wet-dry environment

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 content 0.4wt%, 3wt% and 10wt%). The specimen embedded in epoxy resin was polished down to #800 SiC paper, ultrasonically cleaned and set in a chamber.

The electrochemical measurement of speciment were monitored by the AC impedance method under a cyclic wet-dry condition, which was conducted by exposure to alternate conditions of 1h immersion in a simulated pH10 concrete solution by $(Ca(OH)_2$) containing 0.01M NaCl and 3hour-drying at 298K and 50%RH.

The measurement of impedance at 10kHz(Z_H) and 10mHz(Z_L) with 10mV amplitude was conducted continuously using an FRA with a multiplexer controlled by a computer through the GPIB interface.

3. Results and discussion

3.1 Corrosion rate under wet-dry cycle

Corrosion current density i_{corr} has been calculated by using the Stern-Geary equation.

$$i_{corr} = k/R_P \tag{1}$$

$$k = -b_a b_c / 2.303(b_a + b_c) \tag{2}$$

Where b_a and b_c are Tafel slopes of anodic and cathodic polarization curves respectively. Using these Tafel slopes, the value of k was fixed at 0.02V in this study.[5]

The rate of corrosion was determined by taking impedance of specimen at low frequency, Z_L and at the high frequency, Z_H.

The polarization resistance, R_P was then calculated by subtracting Z_L from Z_H and i_{corr} was obtained from the R_P value using Eq.(1).

Fig. 2 and 3 show the results of the corrosion monitoring for the pure iron and Fe-3wt%Cu subjected to an alternate conditions of 1h-immersion and 3h-drying at 50%RH and 298K over a period of 230h, respectively.

In case of pure iron, the results of R_p^{-1} monitoring show that within each cycle, the i_{corr} increases just after the specimen was submerged in the test solution, and just before the specimen surface dried up in the each stages of wet-dry cycles.

A rapid increase in the corrosion rate just before the specimen surface dried is due to a combined effect of increasing aggressiveness of the electrolyte and oxygen reduction through the thin electrolyte as drying progressed.

On the other hand, Fe-Cu alloys except Fe-0.4wt%Cu showed that corrosion rate is small if the surface shows a with a visibly thick electrolyte layer and during drying, the corrosion rate did not show a pronounced maximum.[6]
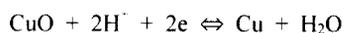
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3.2 Corrosion rate and corrosion potential

3.2.1 Pure iron

The corrosion rate of the pure iron as shown in Fig. 2 was greatly accelerated by the wet-dry cycles. Because the active FeOOH species, which are produced by the oxidation of Fe_3O_4 during drying, act as very strong oxidants to the corrosion of pure iron in wet condition.[7] During subsequent drying, the thickness of the electrolyte layer decreases and oxygen will be reduced at rapid rates on rust layer leading to high corrosion rates.[8] This can be explained by an acceleration of the rates of oxygen transport through the thin electrolyte layers.

3.2.2 Fe-3wt%Cu

The corrosion of Fe-3wt%Cu under the wet-dry cycles is divided into three regions, as shown in Fig. 3. In the initial stage (region I), the corrosion was inhibited due probably to air-formed oxide, which was produced on the alloy surface before experiment. In the region II, the corrosion commenced by onset of breakdown of the air-formed oxide after several wet-dry cycles. The corrosion was accelerated by the wet-dry cycles in this region and the red rust was observed on the surface of alloy. It seems that iron dissolves preferentially into the solution, leading to an increase of copper activity at the alloy surface. In the region III, the corrosion for Fe-3%Cu was retarded very much, while that for pure iron was not inhibited until the final cycle. In Fig. 4, change of the corrosion potentials for Fe-3wt%Cu alloy and pure iron in the 21st cycle (region III) is shown. Immediately before the surface dried up, the corrosion potentials for both specimens shifted rapidly to noble values. It can be seen in Fig. 4 that the corrosion potential for the Fe-3%Cu alloy was much higher than that for the pure iron. This indicates that the reduction of corrosion rate by addition of copper is caused by inhibition of the anodic process rather than the cathodic. This inhibition is attributed to formation of copper oxides. The presence of copper oxides in the rust layer is confirmed from the fact that the corrosion potential for Fe-3%Cu alloy in the immersion remained around -0.2 V (Fig. 4), which is close to redox potential of the following equilibrium;[9,10]

$$CuO + 2H^+ + 2e \Leftrightarrow Cu + H_2O$$

$$E_0 = -0.221V \text{ vs SSE at pH10} -- \text{Eq.} \tag{3}$$

4. Conculsions

In this study the atmospheric corrosion properties of pure iron, Fe-Cu alloys have been investigated for several wet/dry transitions. From experimental results, it could be
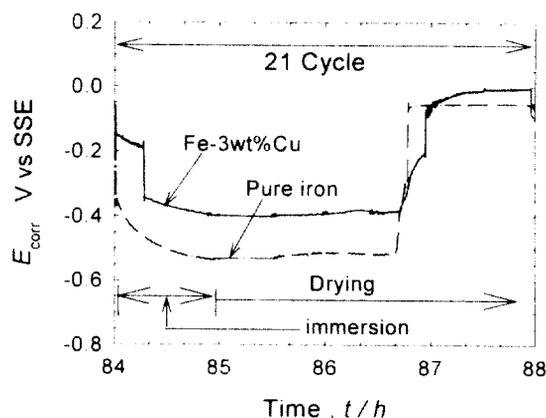

Fig. 4. Change in corrosion potential with time on one wet-dry cycle in Region III.

concluded as follows ;

1) The corrosion rate of the iron is greatly accelerated by the wet-dry cycles. Because the active Fe^{3+} species, which are produced by the oxidation of Fe(II, III) in air during drying, act as very strong oxidants to the corrosion in wet condition. As the drying progresses, iron shows a large increase in the corrosion rate and a shift of the corrosion potential to the positive values. This can be explained by acceleration of oxygen transport through the thin electrolyte layer. In contrast to iron, the Fe-Cu alloys show low corrosion rates and the high corrosion potentials in whole cycles.

2) Differently with pure iron, the experimental results have shown that for Fe-3wt%Cu and 10wt%Cu, the corrosion rate were retarded very much. It is thought that the copper oxides of Fe-3wt%Cu is concentrated in rust layer. But for Fe-0.4wt%Cu, the retarding corrosion rate like Fe-3wt%Cu and Fe-10wt%Cu was not observed.

3) Reduction of corrosion rate by addition of copper is due to inhibition of the anodic process by the formation of copper oxides in the rust layers.

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