Visualization of Coupling Current and Immersion Potential of Iron Surface Corroding Beneath the Ice in the Temperature Cycling under the Freezing Point

Kazuhisa AZUMI1)* and Tatsuki NISHIOKA2)

1) Faculty of Engineering, Hokkaido University, N13W8, Kitaku, Sapporo, 060-8628 Japan.
2) Graduate School of Chemical Science and Engineering, Hokkaido University, N13W8, Kitaku, Sapporo, 060-8628 Japan.

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A test specimen, comprising 100 iron wires of 1 mm φ diameter arranged in a 10 × 10 matrix, was exposed to temperature cycling between 0°C and −20°C. NaCl solution (0.1 wt%) was dropped on the surface to form an ice droplet, and the coupling current of each iron electrode against the other 99 electrodes was measured sequentially to obtain a coupling current map. The average coupling current of 100 electrodes varied with temperature cycling. The coupling current increased at a relative humidity > 65% in the absence of an ice droplet, which was similar to atmospheric corrosion at a room temperature higher than the freezing point. When an ice droplet exists, the coupling current increased with increasing temperature and did not depend on relative humidity. This behavior was interpreted as the formation of a thin solution layer of concentrated NaCl solution at the interface between the electrode surface and ice due to the exclusion of NaCl from the growing ice crystal of pure water. From the coupling current map, the inner area of the iron electrodes beneath the ice droplet tended to be a cathode, whereas the outer and surrounding area tended to be an anode. An open circuit potential map was also measured using a quasi-Ag/AgCl electrode placed on the specimen surface. The potential of the inner area was less noble than the outer and surrounding areas and shifted in a less noble direction with temperature. The ice droplet shrank during the temperature cycling and left rust on the surface.

KEY WORDS: ice droplet of sodium chloride solution; anode-cathode distribution; coupling current.

1. Introduction

Atmospheric corrosion is an crucial parameter for practical steels, particularly in cold, snowy regions where a corrosive environment can become severe because of the snowfall, freezing/melting of ice and snow, and spraying of large amounts of corrosive snow melting agent. Therefore, exposure tests are actively performed for estimating material lifetimes. Furthermore, metal corrosion in cold environment, concrete destruction because of the freezing and thawing of concrete internal water, the construction of surface nanostructures to prevent freezing adhesion, and seawater desalination at the freezing temperature have been investigated recently. However, the corrosion mechanism of steels lower than the freezing temperatures has not been actively studied, even in the environment-controlled laboratory. Furthermore, various methods of corrosion tests are being actively investigated because standard test method for metal corrosion under cold environment has not been established.

In this study, the coupling current method, which has been used to investigate the spatial corrosion distribution, was used to understand the corrosion progression under ice (Fig. 1). Wet corrosion occurs by coupling the anodic oxidation of iron, which emits electrons, and the cathodic reduction consumes electrons. This coupling current between the anode and cathode flows within the iron. The coupling current mapping method can visualize the coupling current distribution on corroding metals by dividing the metal sample into many pieces and measuring the coupling current via an external current meter. This method has been used to investigate non-uniform corrosion, galvanic corrosion, welding corrosion, crevice corrosion, atmospheric corrosion, coating film evaluation and so on. In this study, the time transition of surface coupling current distribution under an ice droplet formed using a 0.1 wt% NaCl aqueous solution was measured using a 100-ch electrode made from iron wires arranged in a 10 × 10 matrix.
2. Experimental

Figure 2 illustrates the test equipment. The specimen was a bundle of iron wires of 1-mm-diameter (Niraco Co., Ltd., purity 99.5%) arranged in a 10 × 10 matrix at 2.54 mm intervals embedded in epoxy resin. After mechanically polishing the specimen cross-section (final finishing using Picard manufactured by Nippon Maryo Kogyo Co., Ltd.) and degreasing, the specimen was fixed in a small environmental cell and placed in a temperature control chamber (Yamato Co., Ltd. model IW223). The environmental cell was not completely sealed and was used to prevent the chamber’s airflow from directly hitting the specimen. A digital camera (an autofocus USB connection endoscope with 5 million pixels), white LED lighting, and temperature/humidity sensor (Sensirion model SHT-35) were attached to the environment cell. All 100 iron wires of the specimen were wired and connected to a 100-ch coupling current measurement circuit comprising an analog relay (MOS-FET), current/voltage converter, 16 bit AD converter, and microcontroller. The temperature cycle in the chamber is (i) 0°C for 1 h, (ii) linear transition temperature for 1 h, (iii) −20°C for 1 h, and (iv) linear transition temperature for 1 h. The temperature inside the environment cell changed with a delay to the set temperature of the chamber. During the temperature cycle, a droplet of 0.1 wt% NaCl aqueous solution was put on the specimen surface at point (i) in Fig. 3, a droplet of 0.1 wt% NaCl aqueous solution was submerged in a water tank (Eyela Co. Ltd., model NCB-2510A). The E im of the iron electrode was measured using an Ag/AgCl R.E. placed outside the water tank, and the temperature of the tank was scanned between 20°C and −20°C at 5°C intervals. A temperature sensor (Analog Devices, ADT7422) submerged in the electrolyte solution in a vial was used to measure the temperature of the electrolyte solution.

3. Result and Discussion

3.1. Coupling Current Transition of the Iron Surface in the Temperature Cycle below the Freezing Point

Figure 3 shows the time changes of the average coupling current iCP (av) of all electrodes, the temperature T in the environmental cell, and the relative humidity (RH) during the temperature cycle test. As described in the experimental section, the T measured by a temperature sensor placed in an environmental cell changed with a delay to the set temperature of the chamber. At point (i) in Fig. 3, a droplet of 0.1 wt% NaCl aqueous solution was put on the specimen surface at T wa = −20°C, and the droplet was frozen after a short time. The droplet evaporated and sublimated as the temperature cycle progressed, shrinking and almost disappearing (ii). Further, the RH of the environmental cell also changed because of the evaporation and sublimation.

Figure 4 shows a typical transition of T–RH cycles. Changes in T–RH trace are described as the following. (a) When the temperature drops, the RH decreases because of moisture condensation. However, at T ≤ −15°C, the condensation efficiency decreases, saturated vapor pressure decreases,
and RH increases slightly. (b) When the temperature increases, RH increases because of the sublimation of ice or evaporation of the liquid phase. (c) The temperature in the environment cell gradually approaches 0°C, while the $T_{\text{set}}$ of the chamber remains constant at 0°C. It is assumed that during the transition from (b) to (c), the chamber condition shifts from heating to a weak cooling operation, and the water vapors in the chamber gradually condense, thereby decreasing RH.

In Fig. 3, minute ice crystals were formed on the surface because of dew condensation even before adding the NaCl solution droplet, and $i_{CP(\text{av})}$ slightly increased because of the condensation to form the surface conduction path. After adding the solution droplet, $i_{CP(\text{av})}$ increased significantly and fluctuated with the $T$/$RH$ as the temperature cycle progressed. The amplitude changed according to the size of the ice droplet and the corrosion progression. Figures 5(a)–5(c)
manipulates the changes in \( i_{\text{CP}(\text{av})} \) for one temperature cycle at the points a–c in Fig. 3. The condition before adding the solution droplet is shown in Fig. 5(a). The \( i_{\text{CP}(\text{av})} \) increased as \( T \) increased and reached around 0°C and decreased when \( RH \) was less than 65%. The relationship between \( i_{\text{CP}(\text{av})} \) and \( RH \) is shown in Fig. 5(a’). When \( RH \) was > 65%, the \( i_{\text{CP}(\text{av})} \) increased, which was consistent with the Tomashov type atmospheric corrosion.\(^{26,27}\) This result shows that the corrosion reaction continues even below the freezing point; further, the surface conduction increasing with \( RH \) as the atmospheric corrosion proceeds above the freezing point.

Figure 5(b) shows the response after the formation of ice droplet. \( i_{\text{CP}(\text{av})} \) increased with increasing \( T \) but did not depend on \( RH \). The peak value of \( i_{\text{CP}(\text{av})} \) was more than an order of magnitude, which is greater than that in Fig. 5(a). \( i_{\text{CP}(\text{av})} \) spiked in the presence of ice droplets when the coupling current on one of the iron wire electrodes transited from the cathode to the anode during the transition from the ice-coated state to melting and drying condition.

Figure 5(b’) shows the \( T \)-dependence of \( i_{\text{CP}(\text{av})} \). \( i_{\text{CP}(\text{av})} \) showed positive dependence on \( T \) under the ice droplet because a thin layer of concentrated NaCl solution was formed at the interface between the ice droplet and electrode; thus a similar \( T \)-dependence was observed as in the aqueous solution. This liquid phase is known as “brine;” it is formed inside the ice and affects various physical properties of the ice.\(^{28}\) As previously stated, the peak value of \( i_{\text{CP}(\text{av})} \) beneath the ice droplets was an order of magnitude higher than that in the absence of ice droplets. Because the ice droplet covered less than half of the total specimen area in this experiment, it is presumed that the ionic conduction current in the thin layer of concentrated NaCl solution beneath the ice droplet became dominant. Therefore, the formation of ice droplets obscured the \( RH \) dependence of atmospheric-type corrosion (Fig. 5(a’)), and the aqueous solution-type \( T \)-dependence became clear (Fig. 5(b’)).

During the temperature cycle, the size of the ice droplet decreased because of evaporation and sublimation, and the ice droplet eventually disappeared. This process can occur because of the direct sublimation from the ice surface and evaporation of water from the salt concentrated solution phase. The evaporation of the liquid phase can also be attributed to liquid diffusion into a capillary in the rust. The behavior after the ice droplet disappears is shown in Fig. 5(c). The basic behavior is the same as in Fig. 5(a). However, because of the concentrated residual salt in the corrosion products on the surface, the \( i_{\text{CP}(\text{av})} \) became larger and the surface ionic conductivity increased. The \( T \)-dependence of \( i_{\text{CP}(\text{av})} \) shown in Fig. 5(c’) demonstrates an atmospheric corrosion-type behavior similar to Fig. 5(a’).

### 3.2. Coupling Current Map Beneath an Ice Droplet

Figure 6 shows \( i_{\text{CP}} \) maps of the coupling current after adding 0.1 wt% NaCl aqueous solution. The current value shown in the figure is \( i_{\text{CP}(\text{av})} \). The specimen surface image and the \( i_{\text{CP}} \) map were combined to the right side images. The center of the ice droplet was the cathode, and the surrounding area was the anode (Fig. 6(a)). Because the temperature was low just after the freezing, the surface reactivity was low, and the \( i_{\text{CP}} \) was minor. The \( i_{\text{CP}} \) map at low temperature in the 3rd cycle after adding the NaCl aqueous solution droplet is shown in Fig. 6(a). The presence of a coupling current in the \( i_{\text{CP}} \) map became obvious because the inside of the ice droplet was the cathode and the periphery was the anode. This result suggests that a thin layer of the concentrated salt aqueous solution formed beneath the ice droplet increases the ionic current. Furthermore, oxygen could not be supplied from the atmosphere to the interface solution beneath the ice droplet, and a hydrogen generation reaction could occur. When \( i_{\text{CP}(\text{av})} \) was large, bubble generation was observed under the ice droplet in the video image.

Figure 6(c) shows the results near 0°C. As the \( T \) increased, \( i_{\text{CP}} \) increased, and the participation of the anodic and cathodic currents became clear. The situation after the ice degenerates is shown in Fig. 6(d). Corrosion products remained on the surface where the ice was present, and the anode current flowed even after the ice had disappeared. The situation after the ice completely disappeared is shown...
in Fig. 6(e). A large $i_{CP}$ continued to flow even after the ice completely disappeared because the corrosion products and residual salts promoted ionic conduction.

These results show that, after the ice disappeared, the coupling current on the surface flowed according to the atmospheric humidity even below the freezing point and increased as the temperature increased. Ionic conductivity was maintained at the iron/ice interface even in the frozen state. Similar results were obtained when Milli-Q filter water was used instead of NaCl aqueous solution, although the coupling current was small. Beneath the ice droplet of the NaCl solution, the inner and the outer area of the droplet acted as the cathode and anode. Hydrogen gas evolution was observed under the ice when the coupling current was large. Finally, iron corrosion could proceed even under freezing conditions.

3.3. Potential Map of the Iron Surface Beneath an Ice Droplet

To measure the immersion potential $E_{im}$ of each electrode during the temperature cycle, a microtube containing a pseudo R.E. comprising Ag wire and Ag/AgCl ink was placed on the specimen surface. The R.E. was connected to the iron electrode via an aqueous solution or ice droplet on the specimen surface. An $E_{im}$ map was measured by sweeping the potential difference between the R.E. and 100 individual iron electrodes. The changes in $T$, $RH$, and $i_{CP} (av)$ during the temperature cycle are shown in Fig. 7. An aqueous droplet was put on the specimen at around 0°C in this experiment. The basic behavior of these parameters was similar to those shown in Fig. 3 without R.E.

Figure 8 shows the specimen surface images, $E_{im}$, and $i_{CP}$ maps corresponding to points a–d in Fig. 7. The white bar on the left side of the images represents the R.E.

(a) After 5.5 ks of solution droplet formation, the surface of a part of the electrodes inside the solution droplet turned slightly yellow, indicating that iron was dissolved. $E_{im}$ was slightly less than $-0.4$ V, and a decrease in $E_{im}$ was observed in the yellow electrode. However, cathodic current flowed on some electrodes inside the droplet in the $i_{CP}$ map, causing their $E_{im}$ to become slightly low.

(b) $T$ decreased, and the droplets froze. At this point, $E_{im}$ was about $-0.4$ V and the $E_{im}$ at the area beneath the ice was lower than the surrounding area. In addition, the fluctuation range in the $E_{im}$ map was smaller than that in (a), and the $i_{CP}$ was small overall.

(c) When $T$ increased to 0°C in the frozen state, $E_{im}$ shifted to a less noble potential of $\sim -0.5$ V beneath the ice. However, as $i_{CP}$ increased, the cathodic current tended to flow toward central part in the ice droplet, whereas the anodic current tended to flow at the outer part of the ice droplet. Furthermore, gas generation was observed beneath the ice droplet, indicating that hydrogen evolution occurred beneath the ice under slow oxygen supply. The electrode potential was insignificantly less noble to cause hydrogen generation. This contradiction may be explained by low accuracy in the potential measurement in the ice medium using the pseudo R.E. Hydrogen generation was observed on steels in the exposure test at room temperature.29

(d) $E_{im}$ became immeasurable when the liquid junction between the R.E. and specimen surface was disconnected because of the sublimation and evaporation of ice during the temperature cycle. $i_{CP}$ was observed under and around the small ice droplets, but the average value of $i_{CP}$ was smaller than (b) and (c).

A cross-sectional view of the $E_{im}$ map near the center of the test piece at different times is shown in Fig. 9. (i) and (ii) were cases at different $T$ beneath the ice droplets. $E_{im}$ was ca. $-0.51$ V at $T = -1^\circ$C (i) and ca. 0.43 V at $T = -19^\circ$C (ii). When the liquid junction was disconnected (iii), $E_{im}$ became unstable. An iron plate was immersed in a 20 wt% NaCl aqueous solution to measure the immersion potential $E_{im}$ to ensure the temperature dependence of the immersion potential of the iron. Although the freezing point of 20 wt% NaCl solution is $-16.3^\circ$C, as mentioned above, the liquid phase exists even at the electrode/ice interface at $-20^\circ$C because the salt is excluded from the ice phase to form a concentrated salt aqueous solution layer. The temperature dependence of $E_{im}$ when the temperature was swept twice stepwise between 20°C and $-20^\circ$C (at intervals of 5°C and maintained for 10 min at each temperature) is shown in Fig. 10. $E_{im}$ shifted to noble side as $T$ decreased; $E_{im} = -0.55$ V at $T = 0^\circ$C and $E_{im} = -0.5$ V at $T = -20^\circ$C. The negative dependence of $E_{im}$ on $T$ (Fig. 10), was similar to the result in Fig. 9, but its value deviated toward the less-noble direction from the value shown in Fig. 9, which is represented by a broken line. This is attributed to difference in the potential measurement through the ice and different corrosion reactions beneath the ice. The potential difference between the pseudo-R.E. and iron...
wires was measured using ice, a thin layer of concentrated NaCl aqueous solution on the ice surface, and the ice/specimen surface interface. Therefore, the potential of the frozen iron specimen could be more intensely dependent on its location (condition) than that of an ordinal uniform aqueous solution. At this point, the \( E_{im} \) obtained in Figs. 8 and 9 is a rough indication of the relative potential of each electrode.

**Figure 11** shows the corrosion model of iron beneath the ice based on the results presented above. Tomashov type corrosion progresses on the surface where ice does not exist, according to the RH trend, same as observed at room temperature. A liquid phase containing concentrated salts excluded from the ice phase can form at the metal–ice interface on the steel surface covered with the ice below the freezing point, and wet corrosion can occur. The inside of the ice tended to be the cathode, whereas the outside of the ice tended to be the anode. Because the oxygen supply to the metal surface under the ice is limited, hydrogen may be generated beneath the ice. In typical crevice corrosion,
the narrow part where oxygen supply is restricted becomes the anode. However, in this study, the surface under ice becomes the cathode. The mechanism of this difference is currently unknown. Ice shrinks because of the sublimation of ice or evaporation of the liquid phase in the temperature cycle below the freezing point, leaving corrosion products on the surface.

4. Conclusion

The following findings were obtained from dropping a 0.1 wt% NaCl aqueous solution onto 10 \times 10 matrix iron electrodes and measuring the coupling current map in the presence of ice droplets formed in a temperature cycle of 0°C – −20°C.

(1) Below the freezing point, an ion current flowed on the metal surface without covering the ice because of the dew condensation (freezing) at RH > 60%. This enables the progress of the atmospheric corrosion depending on RH, as reported above the freezing point.

(2) Ionic current flowed in the concentrated salt aqueous solution layer excluded from pure ice beneath the ice on the metal surface covered with ice. The aqueous solution type corrosion proceeds with positive temperature dependence.

(3) The outer part of the ice droplet formed from the aqueous NaCl solution tended to be the anode, whereas the inner part tended to be the cathode.

(4) The iron electrode beneath the ice had a less-noble potential than the iron electrode that was not covered with ice, and bubble generation, probably hydrogen gas, was observed.

REFERENCES