Dissolution Behavior of Iron in Contact with Frozen Electrolyte Solutions

Minami MAEDA, Nobuo UEHARA and Arinori INAGAWA*

Graduate School of Regional Development and Creativity, Utsunomiya University, 7-1-2, Yoto, Utsunomiya, Tochigi 321-8585, Japan

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Abstract

The dissolution behavior of ferrous ions from a pure iron wire in contact with highly-concentrated salt solutions co-existing with ice was visually analyzed. The dissolved ferrous ions complexed with 1,10-phenanthroline doped in the solution, and the resultant coloration was quantitatively evaluated employing a combination of microscopy and image processing. To provide a dimension-controlled solution area, a microchannel was fabricated in bulk ice, and the highly concentrated solutions were filled therein. The effects of various ionic species on the dissolution behavior were studied. We found that dissolution was significant when the wire was in contact with metal chloride solutions, whereas dissolution was not observed with iodide or bromide salt solutions.

Keywords: Iron, Corrosion, Freeze concentrated solutions, Ice, RGB analysis, Mapping

1. Introduction

Steel materials have been utilized for the construction of a multitude of mechanical objects, including buildings, pipelines, and electrical wires. Because of its strength, steel has been employed even in extreme environments, such as under polar/cryogenic conditions. Under such conditions, ice accretion is a critical issue because it accelerates the destruction of steel materials both physically and chemically. Chemical destruction is usually caused by the corrosion of steel surfaces. In general, ice existing in nature is formed by freezing environmental waters, such as sea and river water, and rain. Because environmental water contains abundant minerals and organic compounds, naturally formed ice is regarded as a frozen aqueous solution. When an aqueous solution freezes, phase separation occurs, leading to the generation of pure ice crystals and a liquid phase wherein the solutes are highly concentrated.1,2) The highly-concentrated liquid phase is termed a “freeze-concentrated solution (FCS)”1. Unique chemical processes have been reported to occur in FCS, including the acceleration of chemical reactions and complexation.3-8) Metal reactions in FCS have also been investigated. Choi et al. reported that the dissolution of ferrous ions from magnetite in an FCS was accelerated when the aqueous media was frozen.9,10) The electrochemical approach by Okada et al. revealed that the dissolution of ferrous ions from magnetite was not driven by a redox reaction but by leakage.11) These pioneering studies suggest that FCSs may provide a chemical platform to accelerate ferrous ion dissolution, indicating that corrosion under cryogenic conditions is also affected by FCSs.

The dissolution behavior of ferrous ions in the FCS were generally evaluated by employing the freeze-and-thaw method, as reported by Choi et al.10) In this method, iron samples are dispersed in an aqueous solution and the mixture is frozen. The mixture is thawed after the reactions, and the solution is analyzed using spectrophotometric approaches. This process is very simple but the outcome is highly sensitive to the experimental conditions, including thawing speed and contamination. Okada et al. employed a voltammetric approach to monitoring the leakage of ferrous ions around probe electrodes. Although voltammetry can be employed to monitor the diffusion behavior

* Corresponding author
E-mail: ainagawa@cc.utsunomiya-u.ac.jp
of ferrous ions, in situ observations have not been achieved. To overcome this issue, our research group has reported a microscopic method for the evaluation of ferrous iron from pure iron wire dissolved in an FCS. The ferrous ions dissolved from the wire were complexed with 1,10-phenanthroline doped in the FCS, and the resulting coloration was observed employing microscopy, followed by quantitative evaluation using an image processing tool. We successfully visualized the dissolution behavior of the ferrous ions in the FCS. However, the amount of dissolved ions was hardly analyzed because the morphology of the FCS was stochastically determined. Thus, it is desirable to standardize the FCS morphology to effectively quantify the dissolved ions and enable kinetic analysis, thereby the elucidation of the corrosion behavior of iron in cryogenic environments.

Herein, a dimension-controlled mimic FCS was employed for the evaluation of ferrous ions dissolved from pure iron wire. A microchannel was constructed inside bulk ice and filled with a salt solution with a concentration that equilibrated the ice/solution interface. The effect of co-existing ions on the dissolution behavior was investigated by altering the doped salt. Herein, FCSs mimicking NaCl, CsCl, RbCl, NaF, and NaI were investigated. The coloration resulting from the complexation of ferrous ions eluted into the mimic FCS was quantitatively observed using a combination of microscopy and image processing techniques.

2. Experimental

2.1 Materials

NaCl, CsCl, RbCl, NaI, NaF, and ammonium acetate were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). 1,10-Phenanthroline was purchased from Dojindo Laboratories (Kumamoto, Japan). Pure iron wire (ϕ = 1.0 mm) and PTFE tubes (ϕ = 1.0 mm) were purchased from Nilaco Corp. (Japan). All aqueous solutions were prepared with ultrapure water purified using PURELAB Ultra Ionic (ELGA Labwater, UK). All materials were used as received.

2.2 Fabrication of microchannels and image acquisition

Microchannels in bulk ice were fabricated as schematically described in Fig. 1. A PTFE tube and pure iron wire were inserted into a glass cell (thickness: 1 mm). The PTFE tube and iron wire were aligned to create a “T-junction”, as shown in Fig. 1(A). The cell was then filled with ultrapure water and frozen in a Peltier unit (PU-50W, Takagi Manufacturing Corp., Japan) equipped with a microscope (BH2-FL, Olympus, Japan). After the water was completely frozen at -5.0°C, the PTFE tube was carefully removed from the bulk ice to fabricate the microchannel. The microchannel was filled with a highly concentrated salt solution. The salt solution was doped with 1,10-phenanthroline (1.5×10⁻³ mol L⁻¹) and acetate-ammonium buffer (0.050 mol L⁻¹, pH 5.0). The dissolution behavior was monitored, and diffusive-reflection microscopic images were captured using a CMOS camera (MU853B, AmScope). The sample was irradiated with white light using an LED light source (Model MIC-209, AmScope, USA) during the acquisition process. The measurement temperature was set to -5.0°C throughout the experiments. The obtained microscopic images were processed using ImageJ software (NIH, USA) to obtain RGB values. Herein, the R values normalized to luminance were utilized to quantitatively evaluate the coloration caused by the complexation of dissolved Fe²⁺ with 1,10-phenanthroline.

3. Results and Discussion

3.1 Fabrication of a microchannel in bulk ice

A microchannel was fabricated using the method described above, and the stability of the ice/solution interface was examined. Fig. 2 shows microscopic images of the mimic FCS containing 1.50 mol L⁻¹ NaCl solution. The concentration of the 

![Fig. 1 Fabrication of a microchannel in bulk ice.](image-url)

![Fig. 2 Stability of the ice/NaCl solution interface.](image-url)
solution was set to equilibrate the solution and ice, as determined was stained with Fe$^{2+}$-1,10-phenanthroline complexes to observe from the reported NaCl-water phase diagram.\textsuperscript{5} The liquid phase the ice/solution interface. The FCS was analyzed immediately after fabrication and after 40 min. The ice/solution interface was stable even 30 min after fabrication. When the FCS was spontaneously generated by the freezing solution, the contact area at the wire/solution interface changed during every experimental session. Nevertheless, in the present method, the contact area was kept as constant as possible throughout the experiments to eliminate its effects on the amount of dissolved ferrous ions from the iron wire.

3.2 Quantitative Mapping of Ferrous Ions Dissolved from Pure Iron Wire in Highly-Concentrated Solutions co-existing with Bulk Ice

Ferrous ions dissolved from a pure iron wire in various salt solutions equilibrated with bulk ice were observed employing microscopy, and the acquired images were processed to obtain a geometrical mapping of the diffused ferrous ions therein. Prior to evaluation, the relationship between the R values and the concentration of ferrous ions was determined. Fig. 3 shows the relationship between the R values normalized based on luminance and the concentration of ferrous ions complexed with 1,10-phenanthroline. The R values increased linearly as the concentration of ferrous ions increased in this concentration range. This result indicates that the normalized R values can be utilized to quantitatively determine ferrous ions in the glass cell.

The dissolution of ferrous ions from the iron wire in the salt solution equilibrated with bulk ice was then quantitatively analyzed. First, we examined the effect of co-existing chloride, bromide, and iodide ions on dissolution behavior. The sodium cation was fixed as the counterion. To allow for equilibration of the ice/solution interface, an image was acquired 10 min after microchannel fabrication. The difference between the R values at each measurement time and that at 10 min ($\Delta R$) was indicative of ferrous ion dissolution after reaching equilibrium. The region of interest (ROI) was set to 32×32 pixels to obtain the R values, and the size of the entire image was 4096×3286 pixels. Fig. 4 shows the microscopic images obtained when the iron wire was in contact with an aqueous sodium chloride solution co-existing with ice. These images were processed using ImageJ software to obtain $\Delta R$ mapping, as shown in Fig. 5. Significant dissolution of ferrous ions was observed 50 min after channel fabrication. We also acquired microscopic images and $\Delta R$ mapping for NaBr and NaI, as summarized in Fig. 6 and Fig. 7, respectively. In contrast to the observations of the NaCl study, dissolution was not substantial when aqueous solutions of NaBr or NaI were in contact with the iron wire. Castro\textsuperscript{13} and Moayed\textsuperscript{14} reported that pitting corrosion occurs to a greater extent when a solution containing halide anions with smaller radii is exposed to steel materials owing to differences in the pitting potentials. However, the effect of halide ions on the anodic dissolution of metals is yet to be understood systematically, as both inhibition and promotion effects on metal corrosion have been reported.\textsuperscript{15,16} Further studies on the effect of halide anions should be
Ferrous ions dissolved from a pure iron wire in various salt solutions co-existing with bulk ice.

Quantitative mapping of ferrous ions dissolved from the iron wire. The contact area was kept as constant as possible throughout the experimental session. Nevertheless, in the present method, the area at the wire/solution interface changed during every spontaneous generation of FCS. The ice/solution interface was stable even 30 min after fabrication. When the FCS was obtained, ΔR mapping, as shown in Fig. 6, of the entire image was 4096×3286 pixels. The ROI was set to 32×32 pixels to obtain the R values of interest. The difference between the R values at the ice/solution interface, an image was acquired 10 min after microchannel fabrication. The NaBr solution equilibrated with bulk ice was then quantitatively utilized to determine ferrous ions in the glass cell. This result indicates that the normalized R values can be used to determine the concentration of ferrous ions after reaching equilibrium. The region of interest was examined by visualization methods, and the acquired images were processed to obtain a geometrical mapping of the diffused ferrous ions therein.

Prior to conducting tests in NaCl solutions co-existing with ice, the microscopic images acquired when the iron wire was in contact with aqueous solutions of alkali metal chlorides co-existing with ice were examined. The results obtained using NaCl, dissolution occurred earlier in the case of KCl, RbCl, and CsCl solutions. Borgmann et al. reported that the metal ion alkalinity influences cathodic depolarization at the active point for corrosion. However, the influence of alkali metal ions on corrosion is still under debate. Although previous studies provide us with a systematic understanding of the effect of co-existing ions on metal corrosion, the present method of in situ visualization would benefit kinetic studies on dissolution for elucidating the mechanism of corrosion under cryogenic conditions.

Interestingly, the dissolved ferrous ions showed spherical diffusion under all experimental conditions. This is attributed to the diffusion process of the reactant, including halide ions and dissolved oxygen, also diffusing spherically toward the pitting point. Thus, if the diffusion process is the rate-determining step of corrosion, the size of the solution phase critically influences corrosion behavior. The present study entails a millimeter-scale contact area, whereas the area arising from spontaneously generated FCS is on a micrometer scale. Thus, planar dimensions may occur when a nano/micrometer-sized FCS is used. In future work, we will report the effect of solution size on the corrosion behavior by controlling the morphology of the FCS.

**Fig. 6** Mapping of ∆R values of iron wire in contact with 1.5 mol L⁻¹ NaBr solution co-existing with bulk ice.

**Fig. 7** Mapping of ∆R values of iron wire in contact with 1.5 mol L⁻¹ NaI solution co-existing with bulk ice.

**Fig. 8** Mapping of ∆R values of iron wire in contact with (A) KCl (1.5 mol L⁻¹), (B) RbCl (1.6 mol L⁻¹) and (B)CsCl (1.8 mol L⁻¹) solution co-existing with bulk ice.
4. Conclusion

A microchannel filled with highly concentrated solutions equilibrated with bulk ice was employed as a platform for evaluating the dissolution behavior of ferrous ions from pure iron wire under cryogenic conditions. In contrast to our previous studies utilizing spontaneously generated FCSs, the effect of the contact area on dissolution was eliminated. The effect of co-existing ions on dissolution behavior was then evaluated. We found that chloride ions play an important role in dissolution even under cryogenic conditions, whereas bromide and iodide ions are less impactful. Our research group is currently establishing a procedure for evaluating dissolution into spontaneously generated FCSs by controlling the morphology thereof and advanced image processing, which will be reported in the near future.

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References