

Corrosion on Steel Surfaces with Sea-Salt Deposition and Artificial Seawater Film

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The conditions to simulate the atmospheric corrosion behavior in the laboratory were investigated to clarify atmospheric corrosion mechanism of steel material in coastal area. For airborne sea salt and artificial seawater droplet, the various behaviors were observed by optical microscope. The particle size of the dried airborne sea salt was about 20 μm , and was about 1/10 compared with the artificial seawater droplet. Though the airborne sea salt represented the same behavior as the thermodynamic water absorption, the behavior of the artificial seawater droplet deviated from the results of the thermodynamic calculation. It is concluded that the water absorption behavior is influenced by the particle size of the dried sea salt. The corrosion behaviors of carbon steels were observed under the deposited condition of airborne sea salt and artificial seawater droplet. The corrosion behaviors showed a different trend, indicating that the corrosion behavior depended on the particle size of the dried sea salt. The corrosion in the actual environment progressed greater than that in the chamber. Furthermore, the summer showed the greater corrosion than the spring. It is found that the corrosion behaviors are attributed to the influence of the environmental factors.

Keywords : *initial corrosion, airborne sea salt, artificial seawater, water absorption process, environmental factor*

1. Introduction

Atmospheric corrosion of metallic materials is a complicated phenomenon, which is influenced by various environmental factors such as temperature, relative humidity, sunshine, rain and airborne sea salt. Especially, because Japan is surrounded in the ocean, airborne sea salt is known to be the most corrosive environmental factor. In order to research the effect of airborne sea salt on atmospheric corrosion, Yamamoto et al. determined the average corrosion rate of carbon steels from the data obtained by five years exposure test, and examined the relationship between the average corrosion rate and the amount of airborne sea salt. They reported that the corrosion rate increases with increasing the amount of airborne sea salt.¹⁾

Most of the research has been carried out by corrosion test under a thin electrolyte layer to clarify the atmospheric corrosion mechanism in coastal area.^{2),4)} However, it is considered that the corrosion behavior in laboratory test,

for example, the corrosion loss etc., is different from that in actual environment. The difference is attributed to the corrosion test that cannot sufficiently simulate the actual environment.

In this study, to clarify atmospheric corrosion mechanism of steel material in coastal area, the conditions to simulate the atmospheric corrosion behavior in the laboratory were investigated. The water absorption behaviors of both airborne sea salt and artificial seawater droplet were examined. Furthermore, the corrosion behaviors of carbon steels were observed under both airborne sea salt deposition and artificial seawater droplet.

2. Experimental

2.1 Airborne sea salt and artificial seawater droplet

Airborne sea salts were collected for two hours in marine site, Oarai seashore of Ibaraki Prefecture. Artificial seawater droplet was prepared by dropping artificial

Table 1. Chemical compositions of the actual seawater and the artificial seawater (wt%)

	NaCl	MgCl ₂	MgSO ₄	K ₂ SO ₄	Others
Actual seawater	78	11	5	2	4
Artificial seawater	68	14	3	2	12

seawater of 5mL weighed by the micropipette. The graphite cleavage plane was used to observe the sea salt particles in a pure surface. The chemical compositions of the artificial seawater used are shown in Table 1. It slightly differs from the compositions of the actual seawater,⁵⁾ but the pH is almost the same, 8.35.

2.2 Water absorption behaviors of both airborne sea salt and artificial seawater droplet

Fig. 1 shows the scheme of the equipment to examine the water absorption behavior of both airborne sea salt and artificial seawater droplet. This equipment allows to observe the sample surface in the cell which controls the relative humidity of an atmosphere by sending the adjusted air. The observation was carried out by optical microscope after 30 minutes, that is, the stabilization of the relative humidity in the cell. Both temperature and relative humidity in the cell were recorded by the thermo recorder.

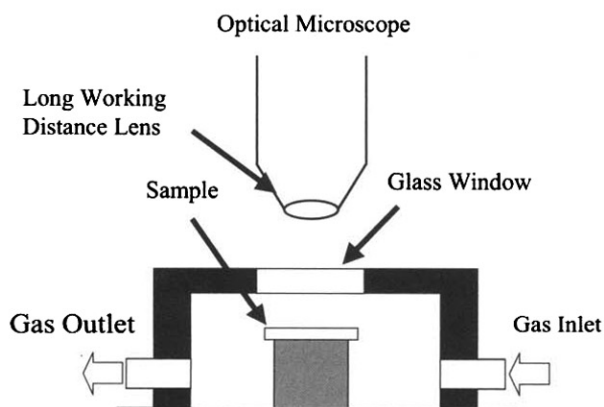


Fig. 1. Scheme of experimental apparatus to examine the water absorption behavior.

2.3 Corrosion behaviors of carbon steels

Carbon steels (JIS SM490A, 50×30×3t mm) were used as samples. The samples were polished with different grades of emery paper down to #1200, and cleaned in alcohol. On the sample surface, the collected airborne sea salt was previously deposited or the artificial seawater of 5 μ L was previously dropped. The corrosion tests were conducted in a chamber set at 30°C and 90%RH and under

the actual environment. The corrosion test under the actual environment was carried out in the summer (2000. 8. 24 ~ 9. 13) and in the spring (2001. 4. 16 ~ 5. 5) by the sheltered exposure test.⁶⁾ There are not the effects of rain in the sheltered exposure test. After the corrosion test, the surface of the samples was observed by optical microscope. Furthermore, temperature and relative humidity of outdoor environment were measured every 5 minutes to study the effect of environmental factors on the corrosion behavior.

3. Results and discussion

3.1 Difference in dried particle size between airborne sea salt and artificial seawater droplet

Fig. 2 shows the optical micrographs of both the airborne sea salt and the artificial seawater droplet at 30%RH. The particle size of the airborne sea salt is almost 20 μ m. The artificial seawater droplet is about ten times as the same particle size as the airborne sea salt. Yamamoto et

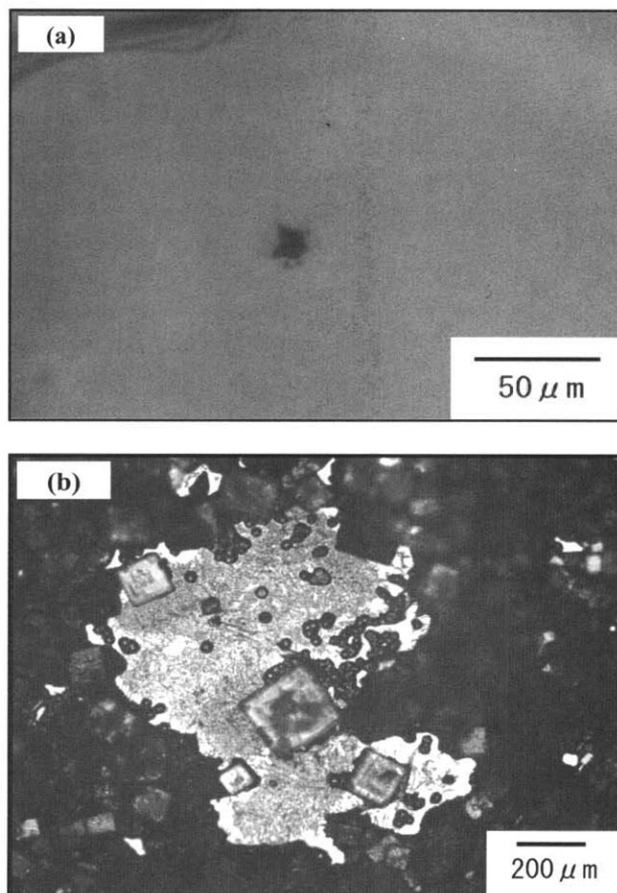


Fig. 2. Optical micrographs of both airborne sea salt (a) and artificial seawater droplet (b) at 30%RH.

al. also observed the airborne sea salt and reported that the average particle size was about $20 \mu\text{m}$.⁷⁾

3.2 Influence of sea salt particle size on water absorption behavior

The water absorption behaviors of both the airborne sea salt and the artificial seawater droplet were observed by the optical microscope, as the relative humidity in the cell was gradually increased from 30%RH. These results are shown in Fig. 3. With increasing the relative humidity, the airborne sea salt began to absorb water gradually from the periphery of the particle and became a perfect droplet at 75%RH. The artificial seawater droplet also showed the similar trend, but the long time was needed to become a perfect droplet even at 80%RH.

The sea salt, which consists mainly of NaCl and MgCl_2 , changes to the solution by water absorption. The concentration is determined by the equilibrium solubility that

changes with the humidity in the air. Yamamoto et al. calculated thermodynamically the amount of absorbed water into the sea salt, on the assumption that the sea salt consisted of NaCl and anhydrous MgCl_2 with the mole ratio, 7.6 : 1. They reported that the sea salt showed the water absorption behavior with each features of NaCl and $\text{MgCl}_2 \cdot \text{H}_2\text{O}$. Thus, the sea salt begins to absorb the water from 32%RH, and at over 75%RH, the much water is absorbed owing to the water absorption of NaCl.⁷⁾

In comparison with the result of Yamamoto et al., the airborne sea salt represented the same behavior as the thermodynamic water absorption. The behavior of the artificial seawater droplet, however, deviated from the results of the thermodynamic calculation, which is attributed to the difference in the particle size of the dried sea salt. It is concluded that the water absorption behavior is dependent on the particle size of the dried sea salt.

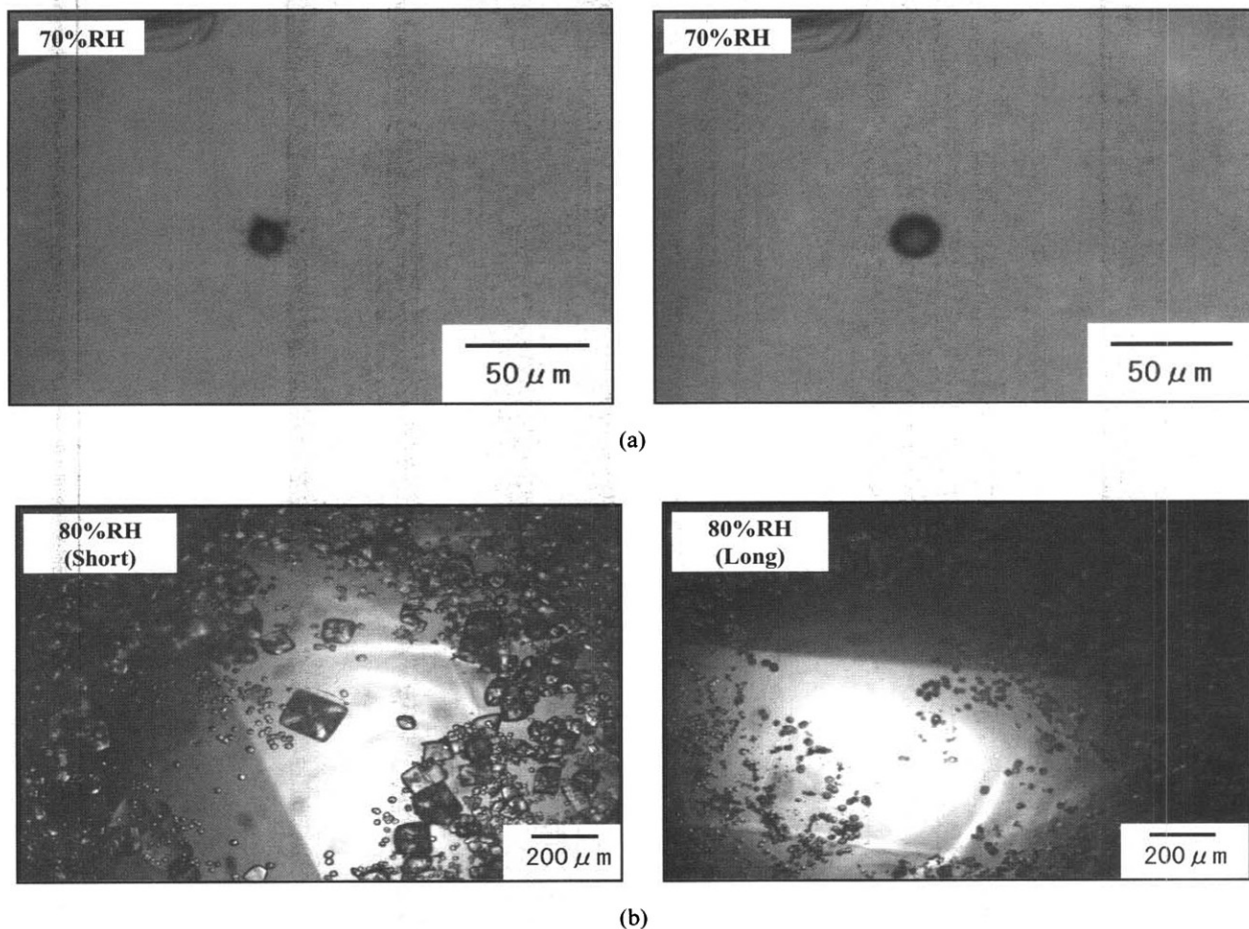


Fig. 3. Optical micrographs of water absorption behaviors at various RH; airborne sea salt (a) and artificial seawater droplet (b).

3.3 Influence of sea salt particle size on corrosion behavior

Fig. 4 shows the results of the corrosion test in a chamber. The deposited airborne sea salt generated filiform corrosion on the carbon after five days, and the growth was observed

on and after ten days. In the case of the artificial seawater droplet, pitting corrosion was generated in the droplet within 1 day. After five days, filiform corrosion was observed in the periphery of the droplet, and the corrosion progressed not only outside the droplet but also inside the

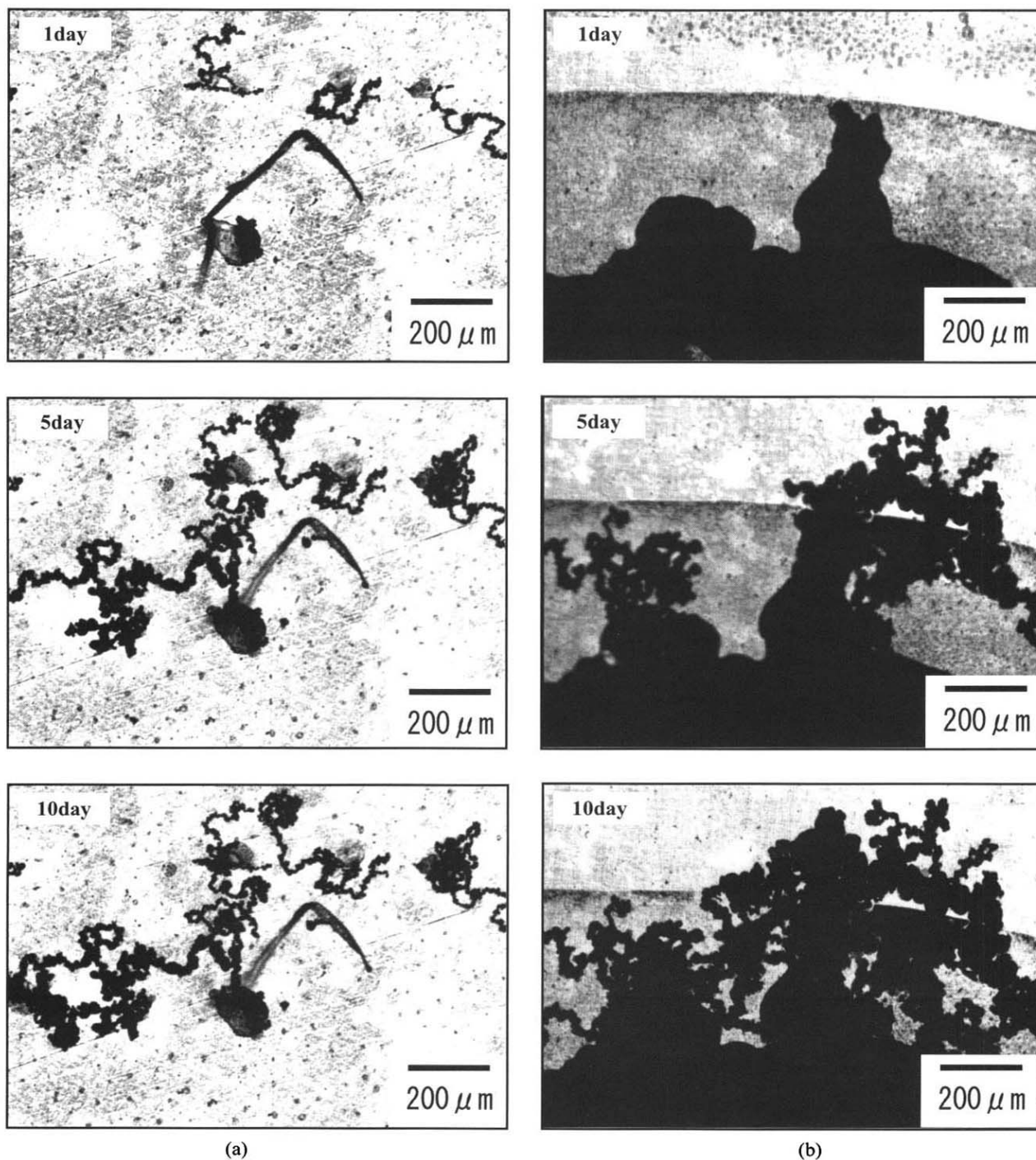


Fig. 4. Optical micrographs of carbon steels with airborne sea salt deposition (a) and artificial seawater droplet (b) after corrosion test in chamber.

droplet on and after 10 days. This is attributed to the difference in the size of the droplet which is dependent on the particle size of the dried sea salt. Especially, it is considered that the corrosion is greatly influenced by the amount or the film thickness of the concentrated chloride solution formed by the water absorption.

From the solubility diagram for the $\text{H}_2\text{O}-\text{NaCl}-\text{MgCl}_2$ system,^{8),9)} authors calculated thermodynamically the water film thickness formed by the water absorption of sea salt. As the result, it was found that the water film thickness is proportional to the amount of deposited sea salt.¹⁰⁾ Because the dried airborne sea salt showed the particle size of about 1/10 compared with the artificial seawater droplet, the electrolyte layer of the latter is estimated to be much thicker than that of the former. Masuda observed the corrosion behavior of pure iron under thin electrolyte layer by KFM, and indicated that the corrosion behavior was dependent on the film thickness of the electrolyte layer.¹¹⁾ The result of this study corresponds to this fact.

3.4 Influence of environmental factors on corrosion behavior

The optical micrographs of the carbon steels exposed to outdoor environment are shown in Figs. 5 and 6, where the airborne sea salt is previously deposited on the carbon steel. Figs. 5 and 6 correspond to the results in the summer and in the spring, respectively. In addition, typical environmental data in the fine day during exposure test periods is also shown in Fig. 7.

In analogy with the corrosion behavior in humidity chamber (Fig. 4), the surface of the carbon steel in outdoor environment (Fig. 5) scarcely changed after one-day exposure test. After five days, however, the corrosion so greatly progressed that it could be confirmed even in the visual observation, and the difference in the corrosion loss increased with increasing the exposure period. In actual environment, the temperature and the relative humidity greatly changed, while the condition in the chamber was fixed at 30°C and 90%RH.

On the other hand, the corrosion behavior in the summer was compared to that in the spring. The corrosion of the former progressed greater than that of the latter. On the environmental factors, the summer showed higher temperature and relative humidity than the spring. From the above result, it was found that the change of the environmental factors greatly affected the corrosion.

Authors monitored the atmospheric corrosion rate of carbon steels by AC impedance method using the corrosion sensor embedded a pair of electrodes in epoxy resin. It was reported that corrosion proceeded with wetting of the sensor surface owing to dew condensation at night

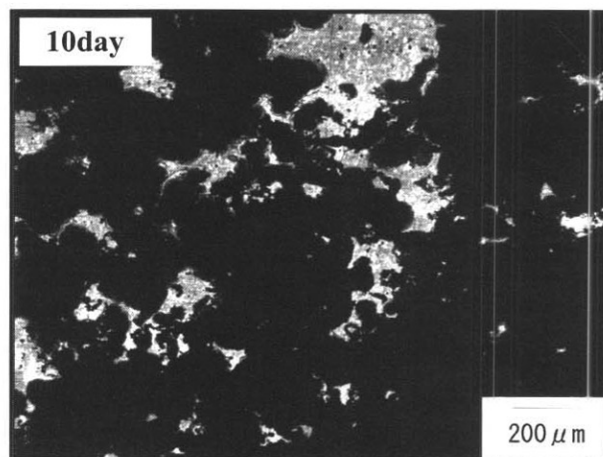
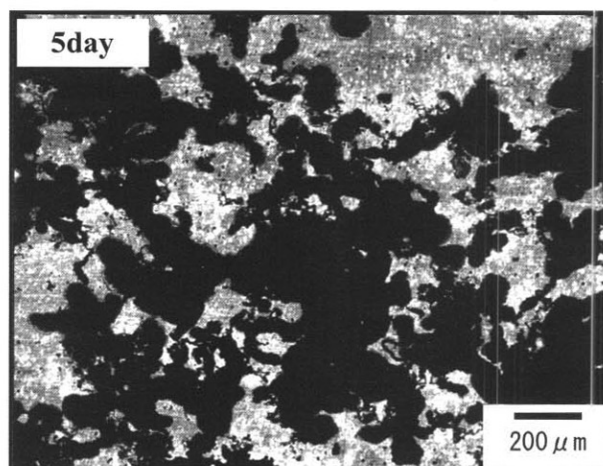
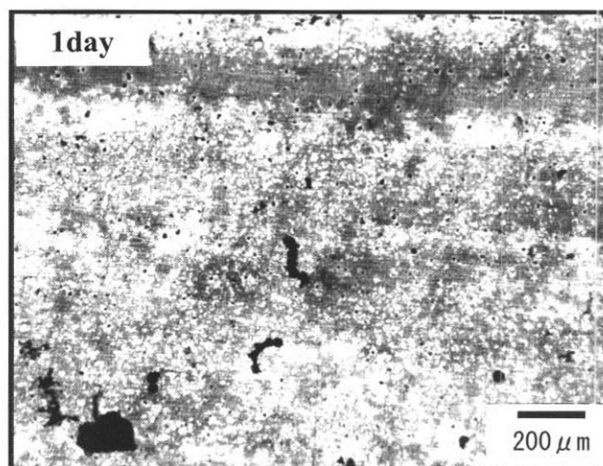


Fig. 5. Corrosion behavior of carbon steels exposed to outdoor environment in the summer.

in the fine day.¹²⁾ Concerning the relation between the time of wetness of the surface and the corrosion, Nishikata et al. indicated that the corrosion resistance depended on the

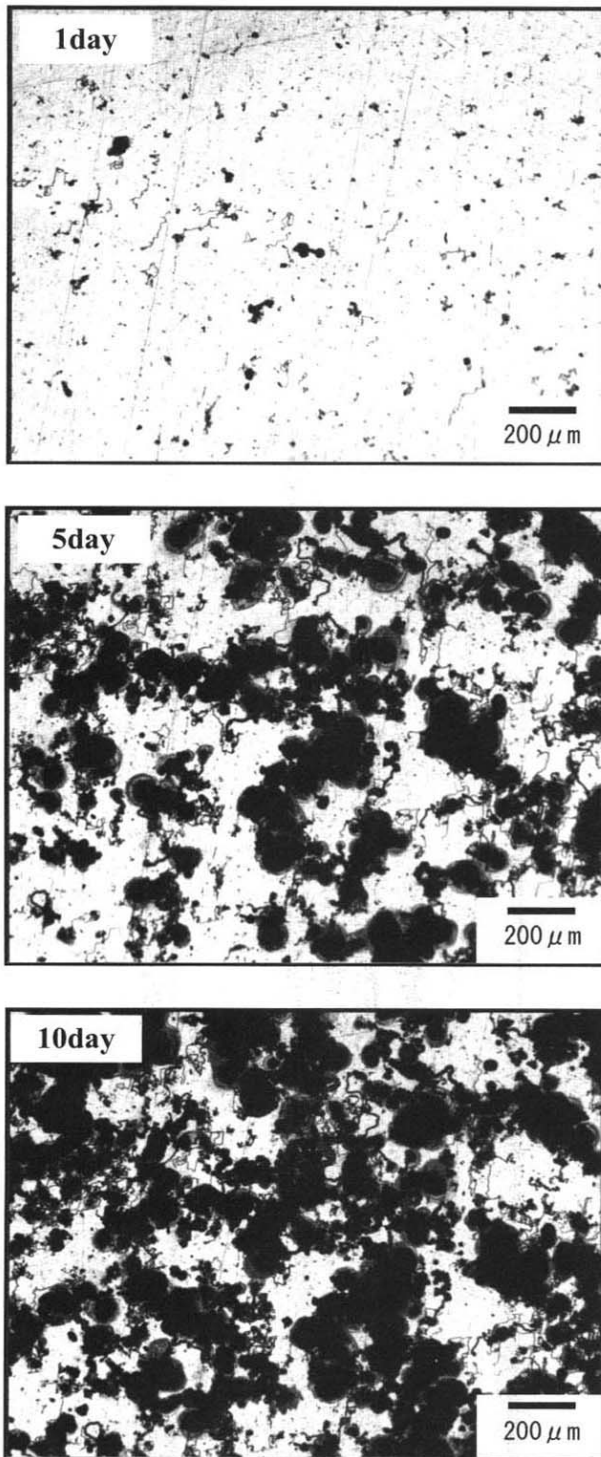


Fig. 6. Corrosion behavior of carbon steels exposed to outdoor environment in the spring.

time of wetness from the monitoring data of low alloy steels.¹³⁾ In this study, the time of wetness in the summer was slightly longer than that in the spring, indicating that

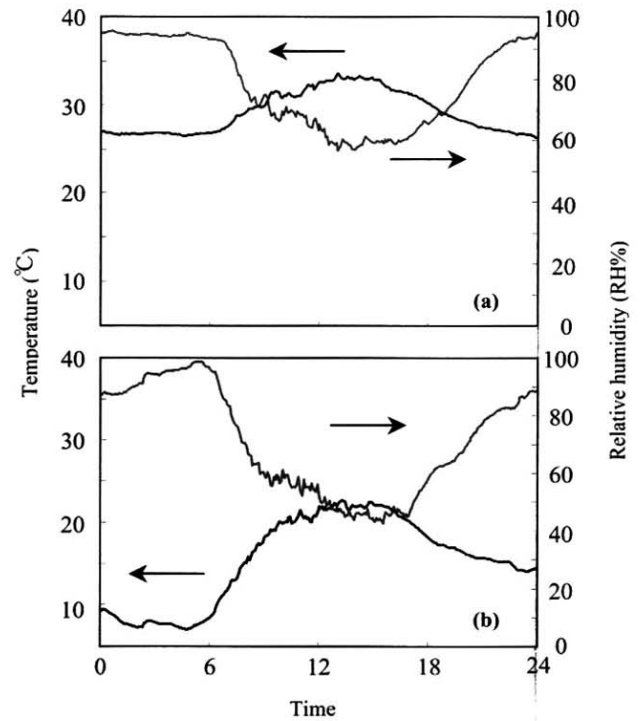


Fig. 7. Change in environmental data in typical sunny day during exposure test periods; in the summer (a) and in the spring (b).

the time of wetness influences the corrosion. In spite of the longer time of wetness in the chamber than in the actual environment, however, the corrosion loss in the former showed less than that in the latter. The reason is not clear, but it is considered that the other factor affects the corrosion.

Since atmospheric corrosion is greatly influenced by various environmental factors, the phenomenon is very complicated. As the other factor which influences on the corrosion behavior, the thickness of the electrolyte layer formed on the surface is considered. Tomashov conceptually explained that the largest corrosion rate appeared at water film thickness of about $1 \mu\text{m}$.¹⁴⁾ In recent years, Stratmann et al. demonstrated that the corrosion rate showed the highest value at about $10 \mu\text{m}$ by the polarization measurement using the Kelvin probe.³⁾ Furthermore, it is also reported that the rust layer (FeOOH), which is caused by the oxidation in the drying process, works in the wetting process as a strong oxidizing agent.^{15),16)}

4. Conclusions

Concerning the airborne sea salt and the artificial seawater droplet, both the water absorption behavior and the corrosion behavior of carbon steels were investigated.

The conclusions were as follows:

(1) The particle size of the dried airborne sea salt was about 20 μm , and it was about 1/10 compared to the artificial seawater droplet.

(2) Both the water absorption behavior and the corrosion behavior of carbon steels are dependent on the particle size of the dried sea salt.

(3) The corrosion in the actual environment progressed greater than that in the chamber. This is attributed to the influence of the environmental factors.

(4) In order to simulate the actual environment in the laboratory, it is necessary that the sea salt of the same size as the airborne sea salt is deposited on the sample and the corrosion test is conducted under the same condition as the actual environment.

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