〈총 설〉

대기부식에 대한 최근 연구동향
-연구 방법과 실험 결과를 중심으로-

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Recent Development on Atmospheric Corrosion of Metals
-Investigation of Method and Some Experimental Results-

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1. Introduction

Atmospheric corrosion is an electrochemical process which occurs in a limited electrolyte layer of which the thickness is alternatively growing and decreasing. The presence of the electrolyte on the corroding surface causes the formation of solid corrosion products on all metals which remain unpassivated for thermodynamic reasons.

The thin electrolyte layer on metal surface is in a state of "internal" change because of temperature and humidity fluctuations. It may therefore be assumed that in view of the high oxygen content of the air and its considerable solubility in the electrolyte layer, its transport to the metal surface to take up electrons by causing the cathodic partial reaction can be the slowest, and hence a rate determining step. A large increase in the corrosion rate occurs during drying, particularly, when the electrolyte layers are very thin.[1~4]

The relatively thick and adhesive layer of corrosion products will affect the path of the corrosion process. The formation mechanism of the corrosion products, their individual corrosion resistance, their content of soluble species, their structure and homogeneity, and their penetrability by corrosive atmospheric components can be particularly important in deciding the course of atmospheric corrosion.

The rate of atmospheric corrosion is strongly dependent on the availability of moisture. Vernon[5] showed that the atmospheric corrosion rate increased rapidly if the relative humidity rose above a certain threshold value, namely the critical humidity, as shown in Fig. 1. Sereda[6] has pointed out that the major species which have been shown to affect atmospheric corrosion are sulphur oxides, hydrogen sulphide, and chloride.

Under real conditions, the thickness of moisture on metal may vary from a few adsorbed molecular layers to the visible moisture layers reaching tens and hundreds of microns. As a result, atmospheric corrosion can be classified as dry, moist and wet atmospheric corrosion.[7]
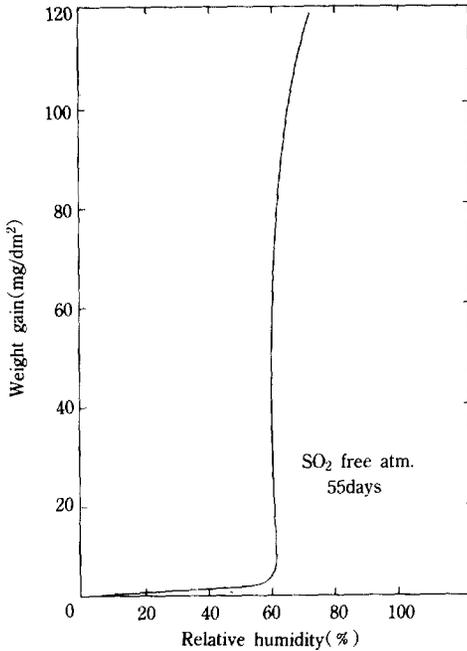
Fig. 1. The relationship between the corrosion rate of iron and relative humidity in an environment containing 0.01% SO₂(from reference[5]).

The velocity of corrosion processes on metals in moist air rapidly increases in the presence of substances capable of ionization in the adsorbed water film. This is connected with the passivity breakdown of metals and the acceleration of the anodic reaction. The rate of metallic corrosion under the visible electrolyte films for the same air pollution is several times higher than that under the adsorbed water layers.

In this paper, the experimental techniques recently developed are briefly brought back to mind and then some experimental results are reviewed.

2. Experimental Techniques

For many years the atmospheric corrosion of metal has been assessed generally by visual inspection and weight loss method which is based on test coupons. The rate of atmospheric corrosion is most frequently studied either by long-term field tests or by accelerated laboratory tests. The field tests are time-consuming and most accelerated tests do not represent the conditions to which materials are actually subjected. In recent years several investigators have attempted to overcome these shortcomings.

Measurement of electrode potential has been suggested as a method of judging the protective quality of rusts formed on metals during atmospheric corrosion.[8] Electrical contact resistance measurement[9,10] and optical reflectance measurement[10] have been used to monitor atmospheric corrosion. An atmospheric corrosion monitor[1,11] has been developed which allows monitoring corrosion behaviour under various atmospheric conditions. Stratmann and Streckel[3,4] presented corrosion potential measurement method of a corroding metal surface by using Kelvin probe without touching the surface and corrosion rate measurement method by measuring the decay of the oxygen partial pressure.

Atmospheric Corrosion Monitor(ACM) − ACM is based on measurement of the current of electrochemical corrosion cells, and thus permits determination of the instantaneous value of the current. Galvanic cells with electrodes of different metals have been used in most investigations up to date.[12] It was known from these tests that climatic factors affect the current of the cells in a manner similar to that in which they influence the rate of atmospheric corrosion. The method is suitable for fast determination of the corrosivity of the atmosphere, and that it is possible to investigate the rate of atmospheric corrosion for the anode material in question. The cells have also been used to determine the total period during which the sur-
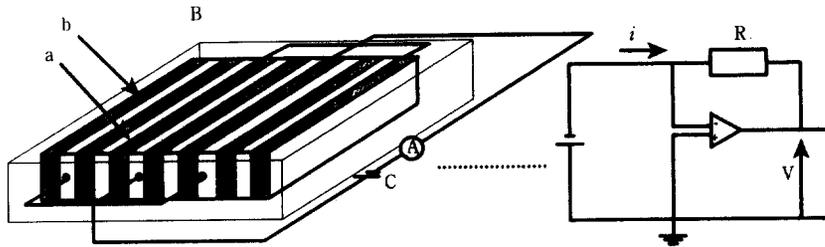
Fig. 2. General arrangement of electrochemical device for measurement of atmospheric corrosion : A is a zero resistance ammeter ; B is an electrochemical cell with (a) electrodes and (b) insulators ; C is an external emf(from reference[12]).

face is covered with a moisture film.[1,11]

ACM was manufactured from metal plates standing on end, each plate separated from its neighbor by a thin mylar insulator. The plates were set in epoxy resin and the surface was machined down to a smooth finish onto which a thin water film was placed. Two types of ACMs have been made—a galvanic cell type and an electrolytic cell type.[12] Their general construction is shown in Fig. 2. The galvanic cell type consisted of alternative plates of two dissimilar metals. This type was used to measure the corrosion resistance of the more anodic metal, and also to give a measure of its ability to protect sacrificially the more cathodic metal. Galvanic current was measured between the dissimilar metal plates with a zero resistance ammeter.

The electrolyic cell type was made of only one type of metal plate in a similar manner to the galvanic cell type. And external electromotive force was imposed on the cell. This is useful in determining the way in which corrosion resistance changes with time t of wetness or pollutant level, and is especially useful for samples with low corrosion rates which could not easily be measured by weight-loss techniques.[13]

Kelvin probe method — A schematic diagram of the Kelvin probe method is shown in Fig. 3. The
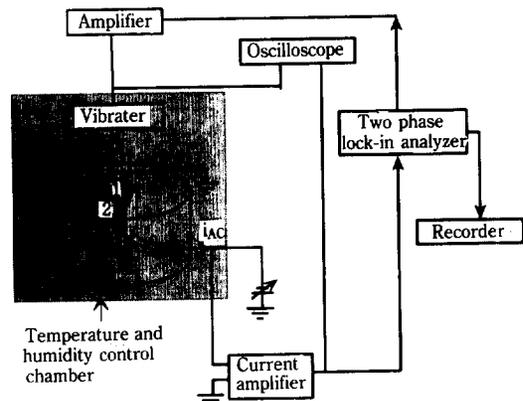
1 : Vibrating reference electrode(pt)
2 : Working electrode(Al alloy)

Fig. 3. Schematic diagram of Kelvin probe apparatus(from reference[3]).

Kelvin vibrating-condenser technique[3,4,14] provides a means of measuring the electrochemical corrosion potential of metals and semiconductors corroding under electrolyte layers produced by contact with humid gases.

1. Vibrating Condenser Theory

The sinusoidal vibration of Kelvin probe with respect to a metal surface produces an alternating current because of the potential difference existing across the gaseous gap between probe and specimen. Let $\Delta\Psi$ be the Volta potential difference. The current i is then given by

$$i = \frac{dQ}{dt} = \Delta\Psi\frac{dC}{dt} \tag{1}$$

, where Q and C are the electric charges on the plate and the capacitance, respectively. For a capacitor with parallel plates of area A, the distance changes sinusoidally with time t as

$$d = d_0 + d_1\sin(\omega t) \tag{2}$$

the capacitance is given by

$$C = \frac{\varepsilon\varepsilon_0 A}{d} \tag{3}$$

, where d_0 is the average distance between the plates, d_1 the maximum amplitude of the vibration, ε_0 the permittivity of a vacuum($8.85\times10^{-12}Fm^{-1}$), and ε the relative permittivity of air. Substituting Eqs.(2) and (3) into Eq.(1) yields

$$i = \varepsilon\varepsilon_0 A\Delta\Psi\frac{d_1\cos(\omega t)}{[d_0 + d_1\cos(\omega t)]^2} \tag{4}$$

and for $d_0 \gg d_1$

$$i = \frac{\varepsilon\varepsilon_0 A\Delta\Psi}{d_0{}^2}d_1\cos(\omega t) \tag{5}$$

If a battery of voltage V is switched into the circuit, then the Fermi levels of both metals differ by the voltage of the battery and i is altered by exactly this amount

$$i = (\Delta\Psi - V)\frac{dC}{dt} \tag{6}$$

When the potential difference is exactly opposed by an applied potential, so that the alternating current vanishes.

2. The Relationship between $\Delta\Psi$ and the Corrosion Potential E_{corr}

The energy necessary to transfer an electron from the electrolyte-covered metal to the vibrating reference metal is identical to zero, as both Fermi levels are equal. This energy can be separated into three terms :

(1) The energy necessary to transfer an electron from the metal into the electrolyte(ΔE_1) :

$$\Delta E_1 = -(\mu_e{}^M - F\Phi^M) + (\mu_e{}^{El} - F\Phi^{El}) \tag{7}$$

, where $\mu_e{}^M$, $\mu_e{}^{El}$ = The chemical potential of the electron in the metal and electrolyte, respectively, and Φ^M, Φ^{El} = the Galvani potential of metal and electrolyte, respectively.

(2) The energy necessary to transfer an electron from the electrolyte into the gas(ΔE_2) :

$$\Delta E_2 = -(\mu_e{}^{El} - F\Psi^{El} - FX_{El}{}^{Gas}) \tag{8}$$

, where Ψ^{El} = the Volta potential of the electrolyte, $X_{El}{}^{Gas}$ = the surface potential of the interface electrolyte/gas.

(3) The energy necessary to transfer an electron from the gas phase into the vibrating reference metal(ΔE_3) :

$$\Delta E_3 = -A^{ref} - F\Psi^{ref} \tag{9}$$

, where A^{ref} = the work function of the reference metal in contact with the given atmosphere and Ψ^{ref} = the Volta potential of the vibrating reference electrode.

As

$$\Delta E_1 + \Delta E_2 + \Delta E_3 = 0 \tag{10}$$

it follows

$$\Delta\Phi_{El}{}^M - \frac{\mu_e{}^M}{F} = \frac{A^{ref}}{F} - X_{El}{}^{Gas} + \Delta\Psi_{El}{}^{ref} \tag{11}$$

, where $\Delta\Phi_{El}{}^M = \Phi^M - \Phi^{El}$ and $\Delta\Psi_{El}{}^{ref} = \Psi^{ref} - \Psi^{El}$

The left hand side of Eq. (11) can be identified

with the absolute half cell potential of the interface metal/electrolyte :

$$\varepsilon_{1/2} = \Delta\Phi_{El}{}^{M} - \frac{\mu_e{}^{M}}{F} \qquad (12)$$

The corrosion potential with reference to standard hydrogen electrode(SHE), is given by

$$E_{corr} = \varepsilon_{1/2} + \varepsilon_{ref} \qquad (13)$$

, where ε_{ref} is a constant half cell potential at the reference electrode/electrolyte interface. It follows from Eqs. (11) to (13)

$$E_{corr} = \left\{ \varepsilon_{ref} + \frac{A^{ref}}{F} - X_{El}{}^{Gas} \right\} + \Delta\Psi_{El}{}^{ref} \qquad (14)$$

In Eq. (14), the work function of the vibrating reference metal, A^{ref}, is a constant for a given environment, and the surface potential at the interface solution/gas, $X_{El}{}^{Gas}$, is assumed to be small, depending a little on the nature of the electrolyte and must be constant for a given electrolyte. Then, the measurable Volta potential difference changes linearly with the corrosion potential of the corroding metal. That is,

$$E_{corr} \approx constant + \Delta\Psi_{El}{}^{ref} \qquad (15)$$

3. Experimental results and discussion

Fig. 4 shows galvanic current(Ig), relative humidity(r.h.) and temperature for the day period using a Cu/Steel ACM. The sharp increase of the galvanic current was observed at evening at which condensation occurred. There is a striking correlation between Ig and r.h., maxima and minima of Ig corresponding to maxima and minima of r.h., respectively. This indicated that thickness of electrolyte affect strongly the corrosion of metals under atmosphere.

Night cycle of the air conditioning system leads to similar fluctuation of Ig, which shows the great sensitivity of ACM to environment. ACM data show briefly the change of corrosion rate during outdoor exposure, and gives information concerning the time-of-wetness and aggressivity of environment.
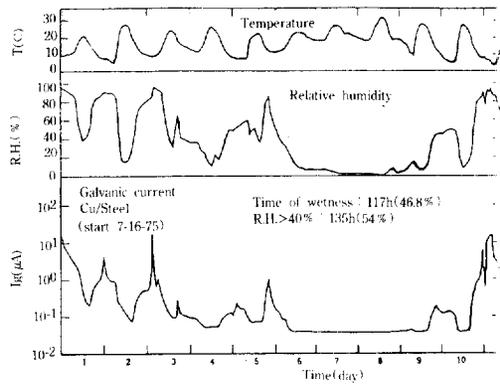

Fig. 4. Galvanic current(Ig), relative humidity(R. H.) and temperature(T) recorded for a 10 day period on the Science Center roof(from reference[1]).
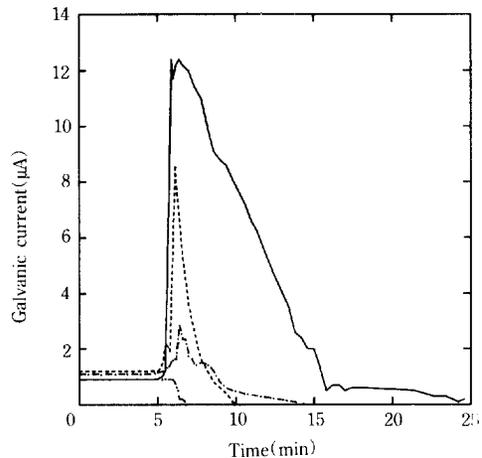

Fig. 5. Transients of the galvanic current obtained during the decrement of aerated electrolyte layer containing different chloride concentrations : —··—, 0M(distilled water) ; —·—, 0.005M ; ----, 0.05M ; —— 0.5M.

In our laboratory,[15] atmospheric corrosion of
Al-1 wt.% Si-0.5 wt.% Cu alloy has been studied
as a function of electrolyte layer thickness in
terms of the galvanic current and the corrosion
potential. The galvanic current for the Al alloy/Pd
galvanic couple and the corrosion potential for the
uncoupled aluminium alloy were measured during
the decrement of electrolyte layer thickness.
Fig. 5 presents the galvanic current resulting from
the Al alloy/Pd couple during the decrement of
electrolyte layer containing various chloride ion
concentrations at a drain rate of $100\sim130\mu m$
s^{-1}. As the Cl^- ion concentration increased, the
larger galvanic current peak was observed. On
the other hand, the galvanic current peak was not
observed for distilled water electrolyte. It is sug-
gested from Fig. 5 that the dissolution rate of
the Al alloy is smaller under chloride ion-contain-
ing electrolyte bulk than under the chloride ion-
containing electrolyte film, while it is higher under
distilled water electrolyte bulk than under distill-

ed water electrolyte film.

Fig. 6 demonstrates the increase in the corro-
sion potential during the decrement of electrolyte
layers containing various Cl^- ion concentrations.
The increase in the corrosion potential goes slow-
er for the electrolyte layer containing higher Cl^-
ion concentration. It is generally known that cor-
rosion potential of metals can be increased either
by promoting cathodic reaction or inhibiting metal
dissolution. In this work,[15] the decrement of elec-
trolyte layer thickness helps to increase the corro-
sion potential either by facilitating the access of
gaseous oxygen through the electrolyte layer and
thus promoting the cathodic reaction, or by
forming the passivity due to the precipitation of
dissolved metal ions for chloride electrolyte layer
or forming the passivity due to oxide film forma-
tion for distilled water electrolyte layer, thereby
inhibiting further metal dissolution. However,
since increasing chloride ion concentration accel-
erates local breakdown of the passivity leading
to a decrease in the corrosion potential, it can
be said that the higher Cl^- ion concentration de-
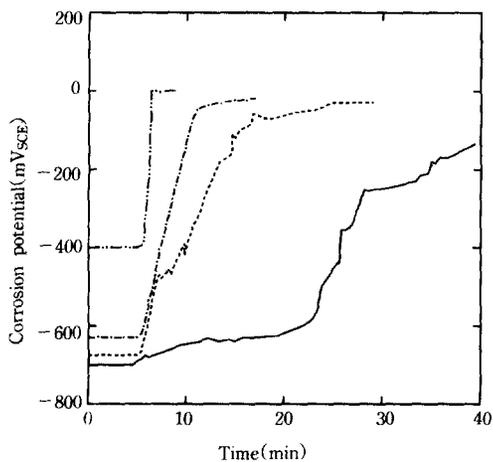celerates more strongly the increase in the corro-

Fig. 6. Transients of the corrosion potential during
the decrement of aerated electrolyte layer contain-
ing different chloride concentrations : $-\cdot\cdot-$, OM
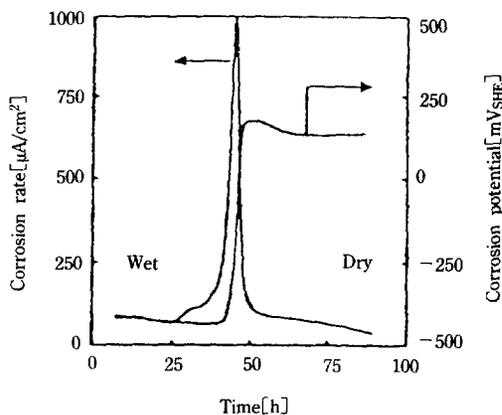(distilled water) ; $-\cdot-$, 0.005M ; $----$, 0.05M ;
$——$ 0.5M.

Fig. 7. The corrosion rate($——$) and the corrosion
potential($----$) during a wet/dry transition of Fe
contaminated by 1g m^{-2} of SO_2 (from reference[3]).

sion potential during the decrement of electrolyte layer thickness.

Fig. 7 presents typical change of the corrosion potential and the corrosion rate for pure iron, as measured with the Kelvin probe and the oxygen consumption technique for a typical wet/dry transition. During decreasing electrolyte layer thickness, the corrosion rate shows a pronounced maximum and the corrosion potential was abruptly shifted to a positive value. A strong correlation was observed between the maximun of the corrosion rate and the shift of the corrosion potential in the positive direction. This provides that the kinetics of anodic and cathodic reactions are determined by the thickness of electrolyte layer.

The Kelvin probe technique has been shown to be applicable to the study on corrosion behaviour of metals covered with extremely thin electrolyte layers. The relative high lateral resolution of Kelvin microprobe makes it possible to measure the local corrosion potential without perturbing the surface condition. The local corrosion potential distribution has not been obtained by using traditional electrochemical methods.

However, the Kelvin probe method is not appropriate in examining the mechanism by which metals lose their passivity due to surface oxide. This is because the method can be applicable only to materials such as metals or semiconductors exhibiting a good electrical conductivity. Thus, in an attempt to elucidate corrosion behaviour of metals under aggressive environments, the conventional methods such as dc and ac electrochemical techniques should be employed in parallel with the Kelvin probe method.

References

1. F. Mansfeld and J. V. Kenkel, *Corros. Sci.,* **16**, 111 (1976).
2. F. Mansfeld and S. Tsai, *Corros. Sci.,* **20**, 853 (1980).
3. M. Stratmann and H. Streckel, *Corros. Sci.,* **30**, 697 (1990).
4. M. Stratmann and H. Streckel, *Corros. Sci.,* **30**, 715 (1990).
5. W. H. J. Vernon, *Trans. Far. Soc.,* **27**, 255 (1931).
6. P. J. Sereda, *ASTM STP,* **558**, 7 (1974).
7. Y. N. Mikhailovsky, "Atmospheric Corrosion", 3rd ed., p.85, Wiley, New York, (1982).
8. P. R. Vassie and M. McKenzie, *Corros. Sci.,* **25**, 1 (1985).
9. O. A. Svedung, *IEEE, CHMT-9,* 300 (1986).
10. R. E. Van de Leest, *Corros. Sci.,* **29**, 507 (1989).
11. F. Mansfeld and J. V. Kenkel, *Corrosion,* **33**, 13 (1977).
12. V. Kucera and E. Mattson, *ASTM STP,* **558**, 239 (1974).
13. G. W. Walter, *Corros. Sci.,* **32**, 1331 (1991)
14. S. Yee, R. A. Oriani, and M. Stratmann, *J. Electrochem. Soc.,* **138**, 55 (1991).
15. S. I. Pyun, S. M. Moon, and E. J. Lee, submitted for publication in British Corrosion Journal (1993).