Water Layer in Course of Corrosion of Copper in Humid Air Containing SO₂

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The technique for *in situ* simultaneous measurements of IR-RAS and QCM, which has been developed for investigation of corrosion in gaseous environments, was employed to study the effects of an extremely thin water layer on the corrosion rate. An evaporated copper film on a QCM element was exposed to air containing water vapor and SO₂, and time-resolved IR-RAS spectra were measured and mass gains were simultaneously followed with QCM. The tested ranges of relative humidity (RH) and concentration of SO₂ were 60% - 90% and 1 - 20 ppm, respectively. On the basis of 2D-IR analysis, the corrosion products were determined to be Chevreul's salt ($CuSO_3Cu_2SO_3 \cdot 2H_2O$) and $CuSO_4 \cdot 5H_2O$. By constructing curves of the relations between band intensities of IR spectra and mass gains of QCM for the corrosion products, the time variations in each product were determined from spectral experiments on copper plates. The thicknesses of physically adsorbed water layers in course of the corrosion process were also determined from water band intensities. The results showed that the thickness of the physically adsorbed water layer increased with increase in RH, and it also increased with increase in accumulation of corrosion products. The latter is probably due to the capillary effect of the corrosion products.

Keywords : in situ measurement, thickness of water layer, corrosion in gaseous environment, copper, SO₂

1. Introduction

Atmospheric corrosion generally proceeds in thin water layers formed on metals in the atmosphere, and the water layer plays significant roles in the mechanism of corrosion and rate of corrosion. Tomashov proposed in a general sense that the corrosion rate increases with decreases in thickness of the water layer to 1 μm and then decreases with further decreases in thickness of the water layer.[1] Turu *et al.* studied the corrosion mechanism and corrosion rate as a function of water film thickness using a Kelvin probe and impedance method,[2,3] and they found that the diffusion limiting current of oxygen increased with decreases in thickness of the water film to around 20-30 μm and then decreased with further decreases in thickness of the water film. They also found that the corrosion rate of copper showed nearly the same behavior as that of the diffusion limiting current of oxygen mentioned above with change in water layer thickness. Turu *et al.*[2,3] investigated a wet/dry cycle of corrosion by using the impedance method, and Stratmann *et al.*[4] investigated such a cycle

of corrosion by monitoring oxygen pressure together with the potential measurement using a Kelvin probe, and they found that there was an abrupt increase in corrosion rate just before drying out.

In the present study, focusing on the effects of extremely thin water layers on the progress of corrosion, a method to determine the amount of water on a corroding surface was developed, and the amounts of physically adsorbed water molecules co-existing with corrosion products were determined. For this purpose the technique of *in situ* simultaneous measurements of IR-RAS and QCM, which has been developed for investigation of corrosion in gaseous environments,[5] was employed, and curves of the relationships of spectral intensities with mass of water on the surface were constructed.

2. Experimental

Evaporated copper films on QCM elements were used as test specimens for simultaneous measurements of IR-RAS and QCM. The QCM element was an AT-cut
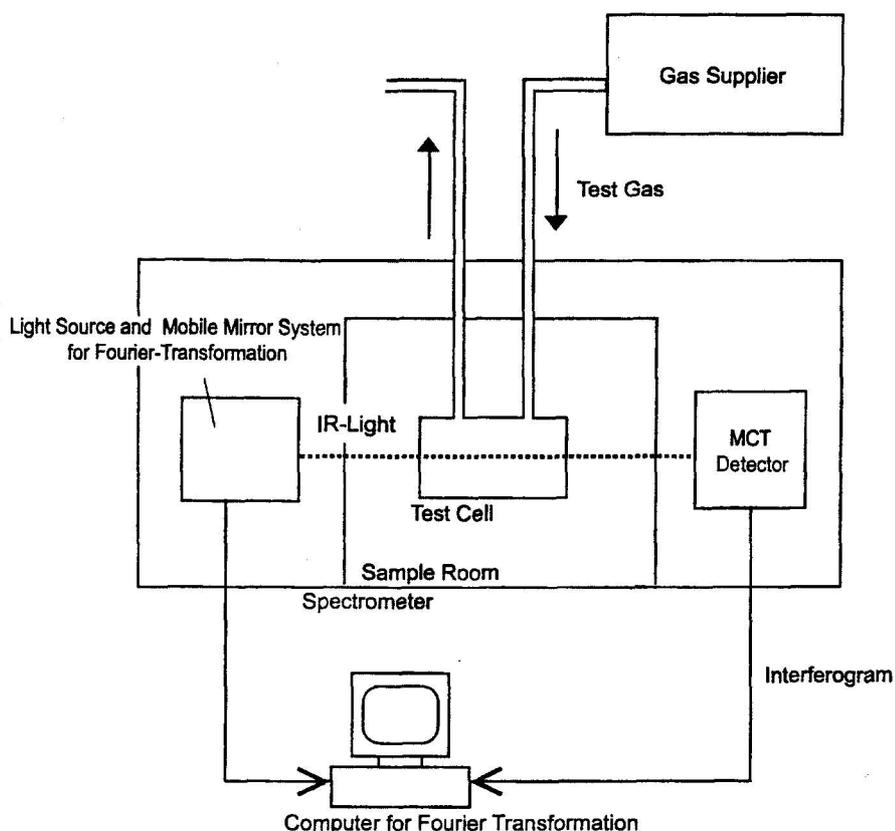
Fig. 1. Apparatus for in situ simultaneous measurements of IR-RAS and QCM.
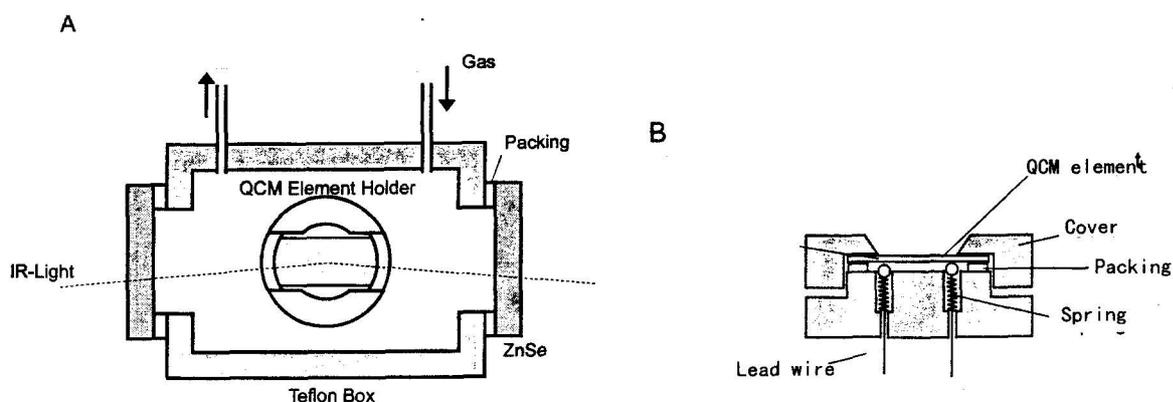

Fig. 2. A: test cell for in situ simultaneous measurements of IR-RAS and QCM. B: side view of the holder for a QCM element.

quartz crystal with a diameter of 1 inch (Maxtek Inc.), and its resonance frequency was 5 MHz. It was exposed to air containing water vapor and SO_2, and time-resolved IR-RAS spectra were measured and mass gains were simultaneously followed with QCM. The apparatus used for the simultaneous measurements, which is composed of a test cell connected to a gas supplier system, an

IR-RAS measurement system and a QCM measurement system, is illustrated in Fig. 1.

The test cell, made of Teflon plates, is schematically illustrated in Fig. 2(A), and a side view of the QCM element holder is illustrated in Fig. 2(B). ZnSe plates were used as optical windows mounted at both ends of the cell. From the results of simultaneous measurement experi-

ments, calibration curves of intensities of spectral bands for the amounts of corrosion products and water layer were constructed.

A copper plate (12x22x1.0 mm) was used as a specimen for the quantitative determination of corrosion products and water layer on the basis of the calibration curves. The tested ranges of relative humidity (RH) and concentration of SO_2 were 60% - 90% and 1 - 20 ppm, respectively. Other details of the experimental set-up and measurement procedure have been described elsewhere.[5]

3. Results and discussion

The time variation in resonance frequencies of QCM evaporated with copper in air with 10 ppm SO_2 and 90% RH is depicted in Fig. 3. As the corrosion gas was introduced into the system at time 0, the frequency steeply decreased at first and then gradually decreased, and a sharp increase in frequency was seen when the corrosion gas was replaced with dry nitrogen gas after a 12.5-hour corrosion test. The mass change corresponding to frequency change is indicated by the axis on the right-hand side in the fig. This variation in mass is explained as the physical adsorption of water for the first steep increase, the accumulation of corrosion products for the subsequent gradual increase, and the desorption of water molecules physically adsorbed on the surface for the last steep decrease.

The spectra simultaneously measured in the course of the above measurements are shown in Fig. 4. Several bands appeared and grew with time. These bands were successfully deconvoluted on the basis of two-dimensional correlation analysis (2D-IR), and the results showed that the peak at around 1050 cm^{-1} was composed of four overlapping bands attributed to Chevreul's salt ($CuSO_3Cu_2SO_3 \cdot 2H_2O$) and copper sulfate ($CuSO_4 \cdot 5H_2O$), the band at around 600 cm^{-1} came from Chevreul's salt, and the peak at around 1640 cm^{-1} was attributed to physically adsorbed water and the crystalline water of Chevreul's salt and copper sulfate.[6] The results also suggested that the mass change indicated by QCM measurements was the sum of mass changes in three components on the surface, that is, Chevreul's salt, copper sulfate and physically adsorbed water.

The spectral change caused by replacing the corrosion gas with dry nitrogen gas is shown in Fig. 5. Spectrum c as shown a negative going peak, which is a difference spectrum between the spectra before (a) and after (b) replacement of the corrosion gas with dry nitrogen, indicates the bands attributed to physically adsorbed water molecules lost by the replacement of the gases. By analy
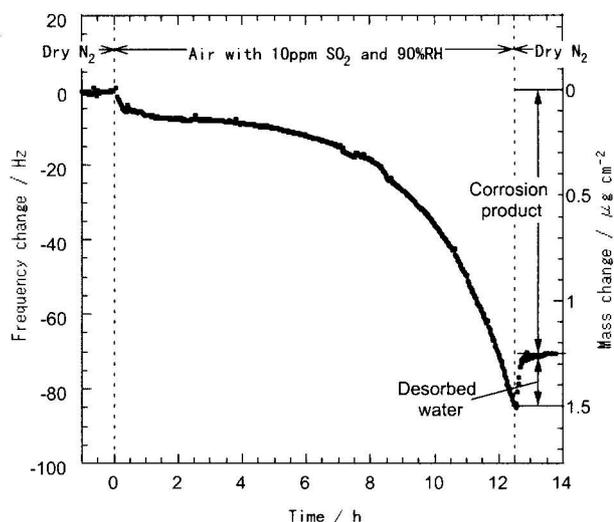

Fig. 3. Time variation in frequency (on the ordinate on the left-hand side) and corresponding mass change (on the ordinate on the right-hand side) of a QCM element covered with evaporated copper in air containing 10 ppm SO_2 and 90% RH.
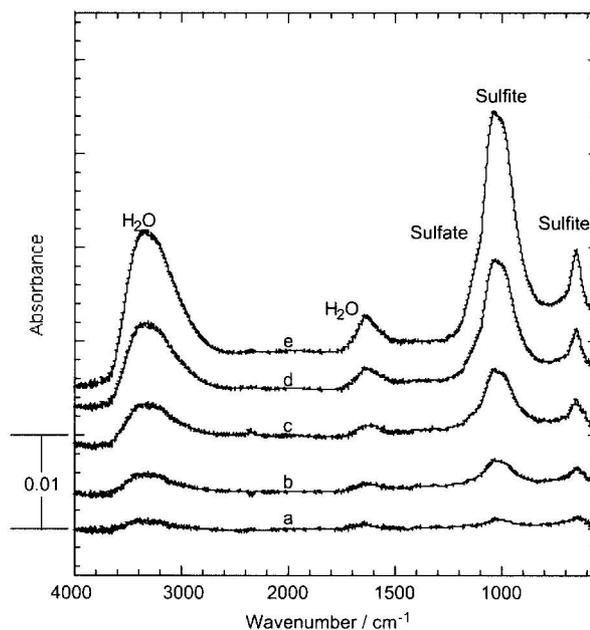

Fig. 4. Time variation in in situ IR-RAS spectra in the same conditions as those described in the legend of Fig. 3. Exposure times were 1 (a), 5 (b), 8 (c), 10 (d), and 12 (e) hours. The reference spectrum was acquired before introduction of the corrosion gas.

zing these negative going peaks, the amount of physically adsorbed water on the corrosion surface can be determined.

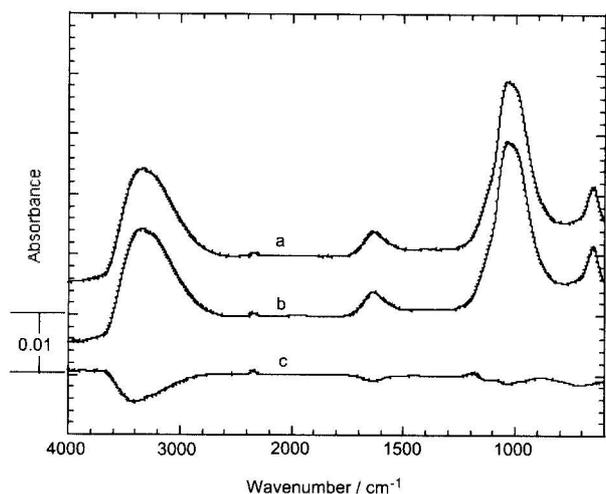By measuring several couples of the band intensities of deference spectra and frequency changes of QCM, the

Fig. 5. Variation in spectra by replacing corrosion gas with dry nitrogen gas. a: 12.5 h exposure to the corrosion gas, which is the same as the corrosion gas used in the experiment for which the results are shown in Fig. 3, b: 1 h exposure to dry nitrogen gas, and c: difference spectrum between a and b (b-a).
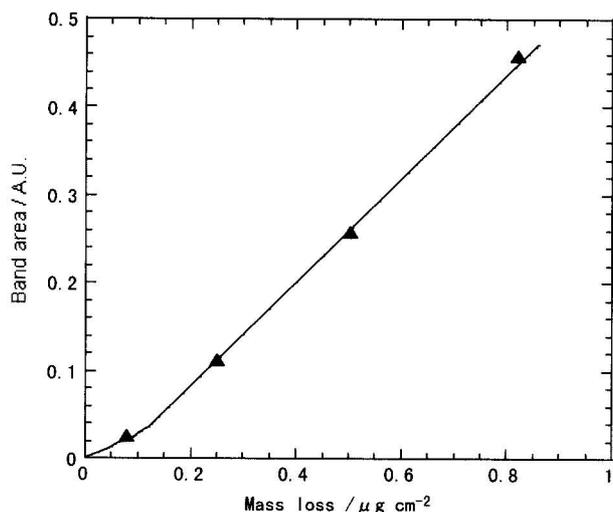

Fig. 7. Relation between amounts of corrosion products and physically adsorbed water on a copper plate in humid air containing 10 ppm SO_2.

Fig. 6. Relation between change in band area at around 1640 cm^{-1} and mass loss by replacing air containing 10 ppm SO_2 and 90% RH with dry nitrogen gas.

relation between mass of desorbed water molecules and band intensities could be determined. The relation is shown in Fig. 6, where the band at around 1640 cm^{-1} of desorbed water molecules was used for calculation of band intensities. The curve shows fairly good linearity except for the range of very small mass change, and it means that we could determine a factor to convert the band intensities to the mass of physically adsorbed water; using this calibration curve we could calculate the amount of water on the surface from spectral measurements like that
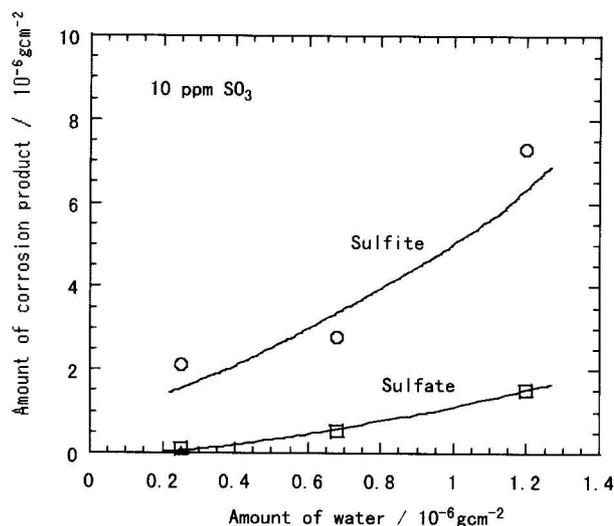
shown in Fig. 5.

The remaining two converting factors for Chevreul's salt and copper sulfate were determined as follows. The band at around 1050 cm^{-1} was deconvoluted to component bands using 2D-IR analysis, and the intensities of the component bands were assigned to each corrosion product. Then we made two simultaneous equations in two unknowns of the converting factors and solved the equations using band intensities and mass changes as variables, the values of which were determined by experiments.

Using the converting factors, the amounts of corrosion products and physically adsorbed water on copper plate specimens were determined from analysis of IR-RAS spectra. The results in humid air with 10 ppm SO_2 are shown in Fig. 7. A comparison of the steep increase just after the introduction of corrosion gas to the system and the steep decrease in the mass at the replacement of the corrosion gas with dry nitrogen gas in Fig. 3 indicates that the physically adsorbed water seems to increase with accumulation of corrosion products. The abscissa in Fig. 7 indicates the amount of physically adsorbed water co-existing with corrosion products, and the mass of physically adsorbed water molecules increased to more than 1.2 $\mu g/cm^2$ with increase in corrosion products, though the mass of physically adsorbed water molecules on a bare surface was less than 0.1 $\mu g/cm^2$ in our experimental conditions.

This difference is probably due to the capillary effect of corrosion products. The corrosion rate is clearly accelerated by an increase in the water layer thickness.

4. Conclusions

By simultaneous measurements of IRRAS and QCM of copper in air containing SO_2 and water vapor, the relations between band intensities of IR-RAS spectra and masses of corrosion products and physically adsorbed water were determined. By using these relations, the amounts of water molecules physically adsorbed on the surfaces of corrosion products were determined. The amount of water increased with increase in RH, and it also increased with increase in accumulation of corrosion products. The latter is probably due to the capillary effect of the corrosion products.

References

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