Efficient Sampling Method for Evaluating Atmospheric Corrosivity Using Sputter-Cleaned Metal Surface

Etsuko Toyoda*, Masamitsu Watanabe*, Mineharu Suzuki**, Hiroshi Ando**, Yasuhiro Higashi***, Toru Tanaka***, Morihiko Matsumoto*, Toshihiro Ichino* and Yoshimori Miyata*

* Technical Assistance and Support Center, Nippon Telegraph and Telephone East Corporation (NTT East)
** NTT Advanced Technology Corporation; Current affiliation of Dr. Suzuki is ULVAC-PHI, Inc.
*** Nippon Telegraph and Telephone Corporation, NTT Energy and Environment Systems Laboratories

We proposed a new efficient sampling method for evaluating atmospheric corrosivity influenced by airborne sea salt and/or pollutants. X-ray Photoelectron Spectroscopy (XPS) was employed to analyze chlorine and sulfur captured in the topmost thin layer of corrosion films. These elements are the main components of airborne sea-salt particles and/or pollutants, both of which promote corrosion. Copper and silver specimens with super-clean surfaces pretreated by Ar- ion sputtering were exposed to three different atmospheres for a period of 1 hour, before and after which they were preserved in a vacuum carrying vessel. XPS was sensitive enough to detect minute amounts of the target elements, which well reflect the atmospheric corrosivity, at the early stages of corrosion. This demonstrates that this method is useful for quick evaluation of atmospheric corrosivity.

Key words: metal plate, sputter cleaning, vacuum technique, X-ray photoelectron spectroscopy, sea salt, corrosivity

1. Introduction

Various corrosive chemical substances exist in the atmospheric environment as aerosol or gas. They not only damage outdoor metal structures, but also can get inside buildings and cause problems for electronic equipments and devices. Evaluating these substances is very important, and various methods have been proposed and studied.1)-6) Automatic on-site analytical methods have already been established for some pollutants such as NOx and SOx, however, analysis for other corrosive substances still depends on ex-situ conventional methods, in which the air sample is collected and then carried to laboratory for analysis. Typically in the sampling process, the air is passed through a filter or adsorption column where the corrosive contents are concentrated. This is cumbersome, and sometimes requires electrically powered equipment. Another method for corrosivity monitoring is based on the exposure of metal coupons over a few months, where prediction of corrosivity is attempted on the basis of the measurements of weight loss of coupons or the measurements of corrosion products thickness by using electrolytic cathodic reduction technique.

One of the most notable substances contributing to atmospheric corrosion is airborne sea-salt particles. Sea-salt particles turn into aerosol and enter buildings or outdoor machine boxes even through their thin gaps. In order to evaluate the effects of sea salt, we had proposed a simple evaluation method, in which copper or silver test pieces were exposed, and then the surface corrosion films were analyzed by X-ray Fluorescence analysis (XRF) and/or X-ray Diffraction (XRD).7)-9) This method is capable of capturing other gaseous corrosive components like air pollutants or H2S. In this method, the sampling is carried out at a designated site by simply hanging metal plates that are cleaned with conventional wet processes, and does not require any special sampling equipment. In addition, the analysis method, i.e., XRF, does not include any wet process, nor does it require a sample pretreatment. We found that the chloride or chlorine ion, the main corrosive component in airborne sea salt, spread into the copper surface oxide layer, and the chlorine content in the surface film had a close correlation with the progress of its corrosion.10), 11) This indicates that the copper plate effectively captures the airborne sea-salt content influencing the corrosion, and this captured chlorine or sulfur does not originate from physically deposited salt.

The typical exposure time was, however, 1 month, and the minimum exposure time required for even the outdoor atmosphere was estimated to be on the order of 1 day. Since the impacts of corrosion-related damage, ranging from building structures to electronic devices and components, increase, demand exists for shorter evaluation time in order to quickly identify the cause of the problems affecting various objects. Furthermore, if evaluation of hourly change in the composition of the atmosphere is possible, we can make more detailed and refined studies on the corrosion environments.

In this letter, we propose a new way to reduce the sampling time of this metal-exposure method to 1 hour for a quicker evaluation of atmospheric corrosivity. We applied vacuum techniques to obtain and keep a metal surface clean: a metal specimen was pretreated with Ar-ion sputtering, and it was kept in a vacuum vessel during transportation to and from the exposure site. By using this clean
metal surface, the corrosion film of early stages, corresponding to a 1-hour exposure, can be characterized. X-ray Photoelectron Spectroscopy (XPS) was adopted to investigate the corrosion layer, which enables us to examine minute substances in this very thin film. Here, we present qualitative results to show the feasibility of this method.

2. Experimental

The copper and silver plates used in this study were 99.99% pure and 5 × 5 × 0.1 mm in size. They were mounted on a sample holder together and covered by aluminum foil that has 2 mm diameter holes at the center of each plate (see Fig. 1). In order to remove surface contaminated and oxidized layers, the plates were sputter cleaned by Ar+ ion of 3 keV in the XPS analysis chamber in a vacuum on the order of 10⁻⁶ Pa. The typical sputtering rate of metals was around 1 nm/min and sputtering was continued until carbon and oxygen were not detected in the XPS spectrum. Next, the metal plates were transferred to the carrying vessel through the load-lock chamber while the vacuum on the order of 10⁻⁵ Pa was maintained. Then, the carrying vessel was detached from the load-lock chamber and carried to the air-monitoring sites.

A photograph of the carrying vessel is shown in Fig. 1. A small, portable battery-driven vacuum pump can be attached to the vessel. At each exposure site, the vacuum valve was first opened and the sample holder was then removed from the vessel. The sample holder was held at a height of 150 cm and good air-circulation to the metal surfaces was achieved. Three sites in Kanagawa prefecture, Japan were selected for the experiment. The first site was a seaside location (Site A; Oiso town, 50 m from the sea), the second side was a roadside location (Site B; Atsugi city, 25 km from the sea), and the third site was a mountainous location (Site C; Atsugi city, 30 km from the sea). The weather conditions of each air-monitoring site are shown in Table 1. After a 1-hour exposure, the sample holder was put back to the vessel, it was then evacuated by the portable pump through the vacuum valve, the valve was closed, and the vessel was carried to the laboratory for XPS analysis. As a reference, the sampling was conducted in an air-conditioned laboratory (Site D; Atsugi city, 28 km from the sea).

The exposed metal plates were transferred to the XPS analyzer without any direct exposure to the atmosphere. XPS analysis was performed with an XPS Analyzer (PHI-5700) in the vacuum under 1 × 10⁻⁷ Pa. The primary X-ray was monochromatized Al Kα X-ray of 200 W. The analyzed area was 800 μm in diameter and spectra between a binding energy of 0 and 1400 eV were measured.

3. Results and Discussion

The air-tightness of the carrying vessel was first evaluated. When the vessel was evacuated by a turbo molecular pump at a load-lock chamber, a vacuum on the order of 0.1 Pa was attained within 1 min (Fig. 2), where the vacuum was measured with the convection gauge. After the vacuum valve was closed and the vessel was detached from the pump, we monitored the pressure. As shown in Fig. 3, even after 10⁴ min (about 6 days), the pressure below 100 Pa is still maintained. Considering the transportation time from the laboratory to the sites and back again to the laboratory was generally expected to be several hours to one day, and with an exposure time of 1 hour, the seal proved to be reliable. The performance of the battery-driven portable pump was evaluated next (Fig. 2). The pressure was reduced to about 300 Pa within 20 s. Quick evacuation after exposure is important for minimizing the effects of moisture and other corrosion-promoting substances during the pumping and upon arrival at the laboratory.

The contamination on the metal specimens during storage in a vacuum vessel was evaluated. After the metal surfaces were sputter-cleaned in a high vacuum, the vacuum valve was closed and the vessel was kept as it was without pumping. Since the sputter-cleaning was carried out until carbon and oxygen were not detected by XPS, the detection of carbon and oxygen contents reflects the adsorption of residual gases like hydrocarbons and water in the vessel. After aging for 1 day in the vacuum, the carbon content
of the copper and silver surfaces increased to 17.2 at% and 25.8 at%, respectively. Hydrocarbons in the vessel are expected to be the main source of carbon contamination, which cannot be prevented completely. Although the carbon contents of the copper and silver surfaces further increased after 14 days of aging, they remained at 32.8 at% and 35.5 at%. For the oxygen analysis, the oxygen contents of copper and silver were 11.0 at% and 4.9 at% after 1 day of aging. The oxygen contents after 14 days of aging were 9.2 at% and 2.2 at%, respectively. Water and oxygen may react with the copper surface to produce ultra-thin oxide film. The fact that the oxygen content rarely changed after 14 days indicates that the surface oxide film did not further grow due to the passive film formation and that fairly stable metal surfaces were maintained. Since the sampling and transportation between the laboratory and sampling sites were conducted within a day, the integrity of the carrying vessel is considered to be reliable for this research.

The XPS spectra for the binding energy of 0 to 500 eV from copper and silver specimens exposed at the laboratory indoor atmosphere (Site D) are shown in Figs. 4 (a) and (b). Although carbon (C 1s) and oxygen (O 1s, not shown in Figs. 4 (a) and (b)) peaks appear, neither a chlorine peak nor a sulfur peak is observed in either of the spectra. The good separation of the laboratory from the outdoor air prevents the intrusion of the sea-salt particles and pollutants, which are thought to be the main origin of chlorine and sulfur. In addition, the relatively long distance, 28 km, from the sea should reduce the atmospheric concentration of sea-salt particles. It is known that it is generally reduced to less than 10% of that of the seaside when the distance from the sea is more than 20 km.12) The corresponding XPS spectra for the seaside site (Site A), which is 50 m from the sea, are shown in Figs. 5 (a) and (b). Chlorine (Cl 2p) peaks are clearly observed on both the copper and silver surfaces. These peaks demonstrate that the sea salt can be caught during a short exposure of 1 hour. Sulfur (S 2p) peaks are also recognized for both the copper and silver surfaces. These peaks are thought to originate from sulfate and/or sulfide ions. Sulfate ion is one of the major sea-salt components, and can also be formed by the oxidation of sulfur dioxide SO2, an important industrial pollutant.13)

The amounts of the captured chlorine and sulfur on the copper surfaces at all of the sampling sites are compared in Fig. 6. Both chlorine and sulfur are detected at all outdoor sites with only a 1-hour exposure. Since chlorine and sulfur contents in the surface film have a close relationship with the progress of corrosion, the evaluation of atmospheric corrosivity may be possible with 1-hour exposures using this method. The chlorine level at the mountainous (Site C) is lower than that at the roadside (Site B), although the distances from the sea are almost the same. Since Site C is in the middle of a large forest area of tall
woods, the airflows from the sea are filtered through the forest to produce clean air, and much of the sea salt can be trapped in the forest canopy. On the other hand, little difference is observed between the seaside (Site A) and the roadside (Site B), although Site A is very close to the sea and much larger chlorine detection is expected there. The chlorine content seems to be saturated on the metal surfaces at both of the sites, and this is probably due to features of XPS analysis. Since XPS analyzes the depth of generally less than ten nm, \textsuperscript{14} which is related to the inelastic mean free path of escaped photoelectrons, the chlorine that permeates the metal surface region beyond this XPS probing depth cannot be detected. Previous studies on the depth-profile\textsuperscript{11} have shown that the chlorine can reach a few micrometers and beyond by a month exposure. Therefore, it is quite likely that the corrosion progressed beyond the XPS probing limit within 1 hour. These results indicate that this method is so sensitive to surface and unsuitable for applying deep corrosions, where XRF may be available complementarily. As for sulfur, similar results are obtained. The reason why the sulfur concentration observed at roadside (Site B) is the highest among all may be due to the effects of heavy automobile traffic.

4. Conclusion

The results presented in this letter demonstrate the high feasibility of the proposed method. It has a high sensitivity to the corrosion-related elements, chlorine and sulfur, and a short sampling time of 1 hour, which is thought to be enough for evaluating atmospheric corrosivity, at least in an outdoor atmosphere. Compared to the conventional method, this is a reduction in sampling time by more than one order of magnitude. This short sampling time combined with the simple sampling scheme even enables hourly monitoring of atmospheric corrosivity. However, the saturation times for chlorine and sulfur to be detected against various environments have to be identified for quantitative monitoring and will be the subject of future research.

In addition, detailed analyses of chemical states using XPS spectra are under way in order to better understand the early stages of copper and silver corrosions.

References


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