Surface Analysis of Copper Patinas Formed Outdoors by using Time-of-flight Secondary Ion Mass Spectrometry

Masamitsu Watanabe*, Takao Handa*, Toshihiro Ichino** and Nobuo Kuwaki*

* Technical Assistance and Support Center, Nippon Telegraph and Telephone East Corporation
** NTT Energy and Environment Systems Laboratories, Nippon Telegraph and Telephone Corporation

We used time-of-flight secondary ion mass spectrometry to get a better understanding of the carbon-containing layer formed in summer and winter on copper exposed to an urban atmosphere. The positive ion mass spectra of as-exposed surfaces revealed that the chemical composition of the carbon-containing layer formed in summer was essentially the same as that formed in winter. However, the intensities of ion fragments originating from volatile organic compounds adsorbed in winter were stronger than those in summer. This is attributed to the temperature dependence of the physisorption of the compounds, assuming that the amounts of hydrocarbon contamination in the analytical instrument were the same for both samples. The positive ion mass spectra of sputtered surfaces (5 nm from the uppermost surface) showed that the chemical composition of the sputtered surface was different than that of the as-exposed surfaces. The only compound found on the sputtered surfaces was dicapryl phthalate (DCP), based on a comparison of the standard mass spectra of DCP with the observed ones. The peaks arising from DCP observed on the copper exposed in winter were higher than those in summer. This is attributed to the higher particulate organic carbon concentration observed in winter. The thicker carbon-containing layer formed on the copper exposed in winter possibly retarded the atmospheric corrosion by acting as a barrier to water adsorption on the copper patina.

Keywords: copper, atmospheric corrosion, carbon-containing layer, time-of-flight secondary ion mass spectrometry (TOF-SIMS), Auger electron spectroscopy (AES)

A carbon-containing layer is commonly found on copper patinas formed during laboratory chamber tests and field exposure.1-3 The origin of this layer has been attributed to hydrocarbon contamination in the chamber of the surface analytical instrument,3 so its chemical composition has rarely been analyzed. Muller and McCrory-Joy reported that copper patinas formed on copper roofs at AT&T Bell Laboratories (40 years of exposure) included several monocarboxylic acids, alkanes, and polynuclear aromatic hydrocarbons, based on gas chromatography mass spectrometry.4 These compounds were extracted from the copper patina by using acetone. Muller and McCrory-Joy suggested that organic compounds possibly acted as an organic binder in the formation and growth of the copper patina and played an important role in its durability.

Graedel et al. reported that atmospheric organic acids such as formic and acetic acid can corrode metals.5 For example, the so-called “bronze disease” is caused by acetic acid emission from wood shavings used as packing materials.5,6 Notoya first demonstrated that localized corrosion in copper tubes occurs when the tubes are exposed to the formic acid vapor.7 The morphology of this corrosion has been described as an “ant nest.” Bastidas et al. showed that formic and acetic acid vapor corrode copper even at low concentrations and that the corrosion rate increases with the acid concentration.8,9 Cuprite (Cu$_2$O), copper hydroxide hydrate (Cu(OH)$_2$·H$_2$O), and amorphous copper formate (in the form of Cu(HCOO) or Cu(HCOO)$_2$) form in formic acid vapor.8 In contrast, cuprite, copper acetate dihydrate (Cu(CH$_3$COO)$_2$·H$_2$O), and copper hydroxide acetate ( Cu$_2$(OH)(CH$_3$COO)$_2$·2H$_2$O) form in acetic acid vapor.9 In short, organic acids affect copper corrosion.

A previous study showed that the corrosion products that form on copper exposed outdoors differ between summer and winter.10 Depth profiling analysis by Auger electron spectroscopy (AES) revealed that the carbon intensity at the surface of the copper exposed in winter was much stronger than that of the copper exposed in summer. The thickness of the carbon-containing layer formed in winter was much thicker than that of the one formed in summer. This thick layer cannot be explained by only the hydrocarbon contamination in the high vacuum analytical instrument. However, the chemical composition of this layer remained unclear.

We have now focused on the carbon-containing layers on the surfaces of the copper patinas of the same samples as in the previous study and analyzed their chemical compositions using time-of-flight secondary ion mass spectrometry (TOF-SIMS). TOF-SIMS is highly sensitive and does not damage the molecular structure of the surface. Notoya et al. used it to analyze benzotriazole (BTA) on copper; BTA is well known to inhibit corrosion on copper.11 However, as far as we know, there has been no reported TOF-SIMS analysis of the carbon-containing layer formed on copper patina exposed outdoors.
As described in the previous report, the samples were 99.9% pure copper plates (42.25 x 0.2 mm). Their surfaces had been cleaned with acetone and nitric acid for degreasing and removal of native oxides, respectively. Then they had been rinsed in deionized water and dried in nitrogen.

Two plates were exposed for one month outside our telephone switching center in Tokyo (site A in the previous report), which is in an urban area. The plates were hung vertically under the eaves of the roof to reduce the effect of rainfall. One plate (Sample A) was exposed from June to July (summer), and one (Sample B) was exposed from January to February (winter), both in 1996. The ambient temperature and relative humidity were continuously monitored; they averaged, respectively, 27.6°C and 65% for the summer period and 8.1°C and 43% for winter one.

The TOF-SIMS analysis was done using a PHI TRIFT II spectrometer under the following conditions. The primary ions were Ga⁺, and their energies for analyzing the positive and negative ions were 12 and 18 keV, respectively. The analysis area was 40 μm square. We analyzed as-exposed and sputtered surfaces. The latter were sputtered to 5 nm from the uppermost surface using Ga⁺ ions. The depth (5 nm) was calibrated using the SiO₂ standard material.

Fig. 1 shows the AES spectra of surfaces of samples A and B. Copper, oxygen, carbon, sulfur, chlorine, and nitrogen were found in both spectra, although the sulfur intensity was very weak for sample B. The measurement by AES was reported in the previous work. This corresponds to the lower amounts of sulfur in the patinas determined by X-ray fluorescence analysis (XRF). The carbon intensity of sample B was much stronger than that of sample A.

As shown in Fig. 2 for the depth profile by AES, the carbon concentration was initially about 30 atomic % at the surface of sample A and rapidly decreased as sputtering proceeded. It was initially about 75 atomic % at the surface of sample B and also decreased as sputtering proceeded, eventually reaching a background concentration at about 80 nm. Similar distributions were previously observed on copper plates exposed at other sites in Tokyo. This indicates that a large amount of carbon species is adsorbed on copper patina surfaces in winter. The carbon-containing layer existed on the copper patinas (mainly composed of cuprite) on copper. As previously reported, cations such as sodium and calcium ions possibly form carbonate, which is found deeper in the carbon-containing layer. However, our target in this study was not the carbonate but the carbon-containing layer at the uppermost surface of the patina.

The previously obtained C 1s X-ray photoelectron spectroscopy (XPS) spectra of the two samples were basically the same, as shown in Fig. 3. One strong peak was found at 284.6 eV and a small peak was observed on the higher binding energy side (peak centered at around 288.5 eV). The width of the main peak for sample A was broader than that for sample B. This is possibly due to the chemical shift of carbon; that is, the peak was composed of several components arising from the chemical bonds between the carbon and the other elements. Each of these components has
a different binding energy; however, the differences are small. The peak on the higher binding energy side originated from the C-O bond. While the C 1s XPS spectra provided the chemical information, it could not determine the molecular species adsorbed on the copper patinas. We thus used TOF-SIMS for that analysis.

Fig. 4 shows the positive ion mass spectra of the as-exposed surfaces. While many ion fragments were found in both spectra, there was almost no difference between the spectra. This indicates that the chemical compounds at the surface of the copper patina on the plate exposed in summer were the same as those in winter. Except for H$_2$O$_{2}^{-}$ (2 amu) and Cu$^{+}$ (63 and 65 amu), almost all peaks originated from volatile organic compounds (VOCs). Typical components were hydrocarbons such as CH$_3$H$_{2}^{+}$ (amu 15), C$_2$H$_3^{+}$ (27 amu), C$_3$H$_5^{-}$ (41 amu), and C$_6$H$_7^{+}$ (55 amu). The alkanes and alkenes are possible origins of these peaks. Two sources possibly account for the VOCs. One is the adsorption of VOCs during the outdoor exposure. The other is hydrocarbon contamination in the analytical instruments. Alkane (C$_n$H$_{2n+2}$) with a high n value is in liquid or solid form. Liquids of VOCs possibly formed particulate matter (PM) or adsorbed on PM in the atmosphere. Therefore, both gaseous and particulate deposition of VOCs must be considered. As described above, there was no significant difference in the chemical composition of the as-exposed surfaces of the two samples; however, the intensities of ion fragments observed on the winter-exposed copper (sample B) were higher than those observed on the summer-exposed copper (sample A). This qualitatively agrees well with the AES results.

The explanation of this difference will be discussed below. Ion fragments originating from carboxylic acids, which corrode copper, were also found. They included CH$_3$O$_2^{-}$ (47 amu) and C$_2$H$_5$O$_2^{-}$ (61 amu). However, their intensities were much weaker than those of ion fragments from other VOCs. This indicates that carboxylic acids are minor components of the carbon-containing layer.

Fig. 5 shows the negative ion mass spectra of the as-exposed surfaces (between 30 and 100 amu). We observed inorganic species such as Cl$^{-}$ (35 amu), NO$_2$ (46 amu), and NO$_3^{-}$ (62 amu). It is interesting that the intensities of the chloride ions were almost the same for both samples although the XRF results revealed significant differences in the amounts of chlorine in the patinas. This is because
the analytical depth of XRF is several micrometers from the surface, while that of TOF-SIMS is several nanometers at most. Actually, the amount of chlorine on sample A was about four times that on sample B. However, the chlorine depth profiles by AES revealed that there was no significant difference in the chlorine concentration at the uppermost surface. As shown in Fig. 6, the chlorine concentrations were slightly above 2 atomic percent for both samples at the uppermost surface (indicated by an arrow in the figure). The agreement between the AES and TOF-SIMS results indicates that TOF-SIMS is a powerful technique for investigating the chemical species on corroded metal surfaces. In contrast, nitrite (NO$_2^-$) and nitrate (NO$_3^-$) were found only on the as-exposed surface of sample A. This agrees well with the AES results, as shown in Fig. 7, which shows the N 1s XPS spectra. Both nitrite and nitrate were detected in the XPS spectra for sample A, although the intensity of the former was very weak. For sample B, a weak broad peak was seen at around 407 eV; however, it could barely be distinguished from the background. A broad peak centered at 399 eV was found in both spectra. As previously reported, this peak can be assigned to ammonium ions (NH$_4^+$), which originate from the deposition of gaseous ammonia and/or particulate ammonium.

Fig. 8 shows the positive ion mass spectra of the sputtered surfaces of samples A and B. Compared to the spectra of the as-exposed surfaces (Fig. 4), the peak intensities were lower, particularly for the smaller mass numbers (hydrocarbons). This indicates that VOCs were mainly at the uppermost surface region, as revealed by the AES depth profile (Fig. 2). A remarkable difference from the spectra in Fig. 4 was the existence of new peaks, which are marked with an asterisk in the figure (211, 229, 453 amu). The peak search program indicated that these new peaks originated from the dicapryl phthalate (DCP)-copper complex. Strictly speaking, copper substituted one hydrogen atom in the DCP, so the mass number shifted to the higher side, 62 amu, which corresponds to the subtraction of the mass of hydrogen from that of copper. Ion fragments originating from the DCP itself, such as 149 and 167 amu, were also found on the sputtered surfaces. This indicates that there was DCP in the carbon-containing layer. The intensities of these peaks for sample B were higher than those for sample A, particularly, for the 453 peak. DCP was thus one of the main components of the inner layer formed on sample B. To the best of our knowledge, there is little information about DCP. However, the properties of dioctylphthalate (DOP), a structural isomer of DCP, are well known. It is a colorless and oily liquid at room temperature and is widely used as a plasticizer. The sources of DOP outdoors are vehicles, PVC manufacturing, and refuse combustion. Since DCP is not a gaseous compound but a liquid, DCP adsorbed as PM on the patina surface, as described earlier. Moreover, it is reasonable that DCP and DOP are abundant in Tokyo, which suffers heavy traffic and has many industrial plants.

The TOF-SIMS analysis revealed that organic compounds such as hydrocarbons adsorbed on the cop-
per patina surfaces. The methane (CH₄) and non-methane hydrocarbon (NMHC) concentrations during exposure are summarized in Table 1. They were recorded at the environmental monitoring station nearest the exposure site. As shown in Table 1, the differences between summer and winter were insignificant. Since gas physisorption decreases as the temperature increases, the high hydrocarbon concentration on the copper surface exposed in winter can be explained by the temperature dependence of physisorption, if we assume that there was no difference in the amount of hydrocarbon contamination in the analytical instruments between samples A and B.

For the DCP detected on the sputtered surfaces, we must consider the organic carbon concentration in the aerosol. The reported organic carbon concentrations in coarse and fine particles at two sites in Tokyo are summarized in Table 2. While these sampling sites were some distance from our exposure site, the differences in concentrations between the two sites were negligible, so it is safe to assume that the concentrations shown in Table 2 are fairly representative of the pollutant level in the analytical instruments between samples A and B.

Table 1 CH₄ and non-methane hydrocarbon (NMHC) concentrations at the environmental monitoring station nearest the exposure site.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average concentration (ppmC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>1.90</td>
</tr>
<tr>
<td>NMHC</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 2 Organic carbon concentrations in fine and coarse particles at two sites in Tokyo.

<table>
<thead>
<tr>
<th>Site</th>
<th>Average concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine</td>
</tr>
<tr>
<td>Koto</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
</tr>
<tr>
<td>Tama</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
</tr>
</tbody>
</table>

As previously reported, the oxide layer thicknesses on samples A and B were 480 and 100 nm, respectively. We attribute this to low temperature, low relative humidity, and low deposition amounts of sulfur and chlorine in winter. Moreover, the thick carbon-containing layer that formed during winter on the copper patina could have retarded the atmospheric copper corrosion by functioning as a barrier to the direct adsorption of water on the patina surface.

The carbon-containing layers formed on copper exposed in summer and winter to urban atmospheres were analyzed by TOF-SIMS. The positive ion mass spectra of as-exposed and sputtered surfaces demonstrated that the chemical composition of the carbon-containing layer did not depend on the exposure season and that it was mainly composed of volatile organic compounds (VOCs) such as hydrocarbons. However, the intensities of the ion fragments from VOCs detected on the as-exposed surface of copper exposed in winter were stronger than those found on copper exposed in summer. This is attributed to the low temperature in winter, which increases the VOC physisorption. The analytical results for inorganic species,
such as Cl\(^-\), NO\(_2\)\(^-\), and NO\(_3\)\(^-\), detected in the negative ion mass spectra agreed well with previous analytical results by AES and XPS. The positive ion mass spectra of the sputtered surfaces (5 nm depth) differed from those of the as-exposed surfaces. Dicapryl phthalate was a typical chemical compound found only on the sputtered surfaces, and the ion intensities from DCP of copper exposed in winter were stronger than those of copper exposed in summer. The higher concentration of organic carbon in winter possibly accounted for this result. The thicker carbon-containing layer formed on copper exposed in winter functioned as a barrier to water adsorption on the copper patina. This is another possible factor accounting for the lower corrosion rate.

We thank Motoki Takahashi of ULVAC-PHI and Hiroshi Ando of NTT Advanced Technology Corporation for assisting with the TOF-SIMS analysis and their helpful suggestions.


(Manuscript received November 28, 2005; in final form February 16, 2006)