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論 文

Comparative XPS Study of Silver and Copper Surfaces Exposed to Flowing Air Containing Low Concentration of Sulfur Dioxide

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Sulfur dioxide (SO_2) is a typical gas affecting the atmospheric corrosion of metals, particularly outdoors. Although many studies have investigated the effect of SO_2 on the atmospheric corrosion of silver and copper, little is known about the early stage of their corrosion behavior. In this study we analyzed the chemical state of sulfur on silver and copper plates exposed to flowing air containing low concentrations (18 and 148 ppb) of SO_2 using X-ray photoelectron spectroscopy (XPS). The shapes of the spectra were the same for both concentrations, indicating that the chemical state of the analyzed elements did not depend on the SO_2 concentration. There was a difference in the chemical state of the sulfur between the silver and copper. Three peaks were observed in the S 2p XPS spectra for the silver originating from bisulfite, $S_2O_5^{2-}$, $S_2O_3^{2-}$, and S^{2-}. The bisulfite resulted from SO_2 dissolution into the surface electrolyte, and the others resulted from the reduction of sulfurous acid. In contrast, only bisulfite was observed in the S 2p XPS spectra for the copper. It also originated from the dissolution of SO_2 into the surface electrolyte. The difference in the chemical state of the sulfur between the silver and copper is attributed to the presence of native oxides on the surface, which may have impeded the reduction of bisulfite.

Key words : silver, copper, atmospheric corrosion, sulfur dioxide, X-ray photoelectron spectroscopy (XPS), chemical state analysis

1. Introduction

Sulfur dioxide (SO_2), a typical gaseous compound found in the atmosphere, corrodes metals, particularly outdoors. When SO_2 adsorbs on the surface electrolyte, it easily dissolves, resulting in the formation of protons (H^+) and bisulfite ions (HSO_3^-). The former reduces the pH of the surface electrolyte, which promotes metal dissolution.

Silver and copper are commonly used in the electronic components and devices typically found in telecommunication equipment. Since silver and copper are affected by SO_2, it is important to know the effects of SO_2 on their corrosion behavior to predict the life expectancy of the equipment. Such knowledge would also be useful for coping with anomalous situations, such as volcanic eruptions, in which the SO_2 concentration can exceed several hundred ppb. A previous study showed that silver and copper plates exposed to the atmosphere were severely corroded following the volcanic eruption on Miyake Island in 2000.1)

Much effort has been expended on clarifying the effects of SO_2 on atmospheric silver and copper corrosion. A number of laboratory experiments have been reported regarding the effects of exposure to high SO_2 concentrations.2)-15) Using infrared reflection absorption spectroscopy (IRAS), Persson and Leygraf showed that sulfite formed on the surface of copper during the initial stage when it was exposed to 0.21 ppm SO_2 in flowing air at 80% relative humidity (RH).16) In situ analysis using IRAS and a quartz crystal microbalance by Ito et al.17)-18) revealed that sulfite-like $CuSO_3Cu_2SO_3 \cdot 2H_2O$ (Chevreul's salt) and sulfate $CuSO_4 \cdot 5H_2O$ formed as corrosion products on copper exposed to flowing air containing 10 ppm SO_2 at 80% RH. Moreover, the formation rate of sulfite was higher than that of sulfate in the very early stage.17)-18) In contrast, the sulfidation rate by SO_2 for silver is much lower than that by reduced sulfur species, such as H_2S and COS.12) Since SO_2 is considered to be a weak corrosive agent for silver, the effect of SO_2 on atmospheric silver corrosion in the initial stage has received little attention.

In this study, the chemical state of the sulfur was investigated when silver and copper plates were exposed for one hour to flowing air containing low concentrations of SO_2. Since the electrochemical reactions occur at the metal/electrolyte interface in the early stage of corrosion, X-ray photoelectron spectroscopy (XPS) was used. The SO_2 concentrations were 18 and 148 ppb ; the former is at least one order of magnitude lower than those in previous studies.16)-18)

2. Experimental

2.1 Exposure

The silver and copper plates were 99.99% pure and 5×5×0.1 mm in size. Their surfaces were sputtered with 3-kV Ar^+ ions to clean them. The sputtering was conducted until both carbon and oxygen were not detected in the XPS spectra, as described elsewhere.19)

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The plates were exposed to flowing air containing two different SO_2 concentrations, 18 and 148 ppb, for one hour. These concentrations are one and two orders of magnitude higher than those observed outdoors in Japan in areas without strong emission sources. The temperature and RH during exposure averaged 26℃ and 44%, respectively. Following exposure, the plates were immediately returned to their carrying case[19] to avoid further contamination.

2.2 Analysis

Using a PHI 5700 photoelectron spectrometer, we analyzed the chemical states of the sulfur, oxygen, and base metals (silver and copper). The X-ray source was a monochromated Al Kα with a characteristic energy of 1486.6 eV ; its total power dissipation was 200 W. Detailed scans of the Ag 3d, O 1s, and S 2p regions for silver and the Cu 2p, O 1s, and S 2p regions for copper were recorded in 0.1 eV energy steps. The spectra were collected at a 45° photoelectron takeoff angle. The binding energies were corrected using that for the adventitious carbon peak at 284.6 eV.

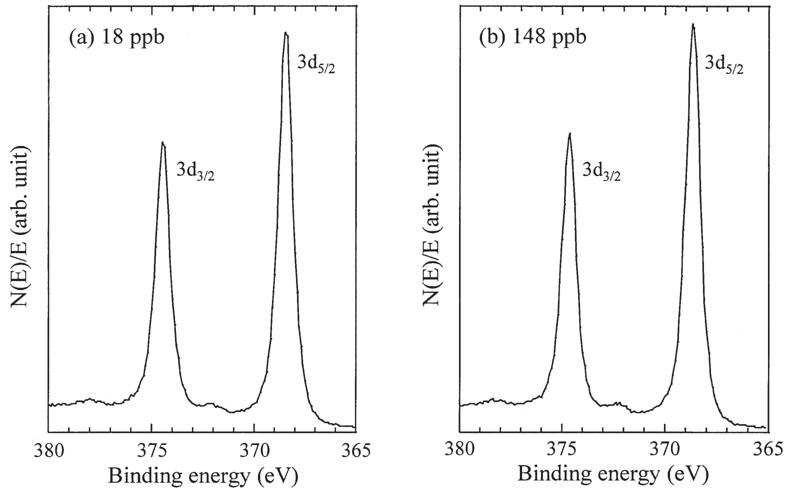

Fig. 1 Ag 3d XPS spectra of silver exposed for one hour to flowing air containing (a) 18 and (b) 148 ppb SO_2.

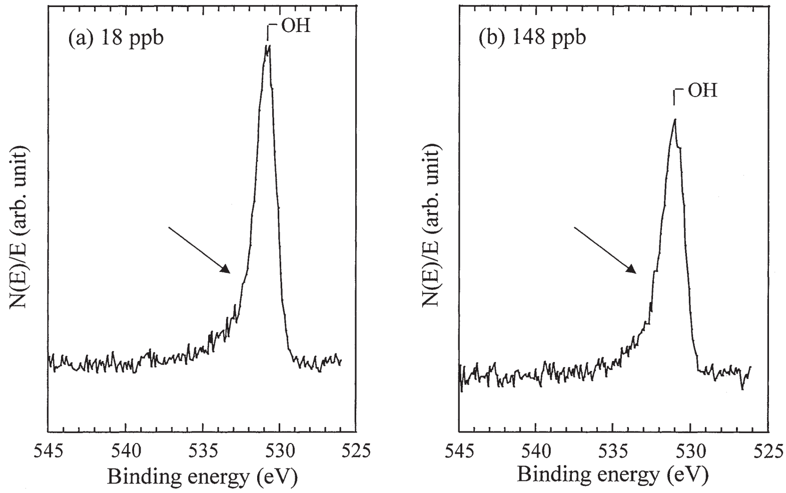

Fig. 2 O 1s XPS spectra of silver exposed for one hour to flowing air containing (a) 18 and (b) 148 ppb SO_2.

3. Results and discussion

3.1 Silver

As shown in Fig. 1, the Ag 3d XPS spectrum for silver exposed to the 18 ppb SO_2 was substantially the same as that of the silver exposed to 148 ppb SO_2. There are two sharp peaks originating from Ag $3d_{5/2}$ and $3d_{3/2}$, the former centered at 368.5 eV and the latter at 374.5 eV. The peak shape, the binding energy difference between $3d_{3/2}$ and $3d_{5/2}$ (Δ), and the peak position of Ag $3d_{5/2}$ (368.3 eV) agree well with those for metallic silver in the Handbook of X-ray Photoelectron Spectroscopy.[20] This means that the silver still had its metallic characteristics even after the exposure.

As shown in Figure 2, the O 1s XPS spectra for the silver were also substantially the same. The peak at 531 eV corresponds to oxygen in hydroxyl (OH).[21] The asymmetric shape of this peak indicates the presence of another component on the higher binding energy side (indicated by the arrows in Fig. 2). This component originated from the oxygen in the bound water (H_2O).[21] The presence of these two components in the O 1s XPS spectra indicates that water in the atmosphere (the average RH was 44%) adsorbed on the silver surface. Components originating from the silver oxide (Ag_2O), which has a binding energy of 529.2 eV[20], were not observed. This is reasonable because silver oxide does not form under ordinary conditions, unlike copper oxide.[22] These results agree well with those reported by Kim and Payer.[23]

As shown in Fig. 3, the S 2p XPS spectra for the silver were also substantially the same. There are three components arising from the S $2p_{3/2}$: a broad peak at around 162 eV and two sharp peaks at 165.9 and 167.5 eV. The shoulder observed on the higher binding energy side for both concentrations is attributed to the S $2p_{1/2}$ component of the peak at 167.5 eV given the difference in the binding energy between S $2p_{1/2}$ and S $2p_{3/2}$ (1.18 eV[20]). Table 1 summarizes the binding energies for the reference compounds.[6), 10), 24)] The broad peak at 162 eV originated from S^{2-} or $S_2O_3^{2-}$. The peak at 165.9 eV originated from $S_2O_4^{2-}$ or $S_2O_5^{2-}$. Both ions have two sulfur atoms and one more peak, as shown in Table 1. There are four possibilities for the strongest peak at 167.5 eV : sulfite (SO_3^{2-}), bisulfite, $S_2O_3^{2-}$, and $S_2O_5^{2-}$. During exposure, SO_2 dissolved into the surface electrolyte and bisulfate ions formed, as described above; therefore, the peak at 167.5 eV mainly

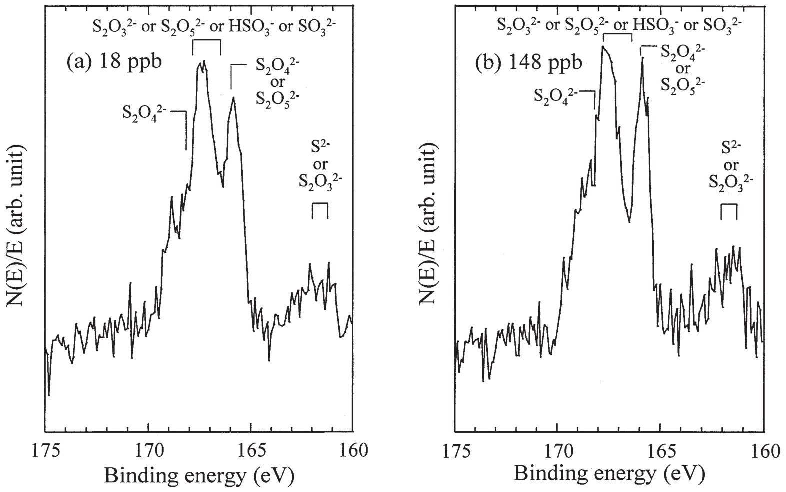

Fig. 3 S 2p XPS spectra of silver exposed for one hour to flowing air containing (a) 18 and (b) 148 ppb SO_2.

Table 1 Sulfur $2p_{3/2}$ binding energies for reference compounds.

Compound	Binding energy (eV)	Ref.
$NaHSO_3$	166.7, 167.4	10)
Na_2SO_3	166.5	6)
$Na_2S_2O_4$	166.1, 168.2	10)
$Na_2S_2O_5$	166.0, 167.5	24)
$Na_2S_2O_3$	161.8, 167.9	10)
	161.3, 167.2	24)
Cu_2S	161.8	10)
	162.0	6)
$CuSO_4$	168.9, 169.2	6)

originated from bisulfite. The peak at 165.9 eV apparently originated from $S_2O_5^{2-}$ because the binding energies of two peaks shown in Table 1 correspond to the observed ones. The existence of a lower sulfur valence state (S^{2-} or $S_2O_3^{2-}$) indicates the reduction of sulfur.

3.2 Copper

Fig. 4 shows the Cu 2p spectra for the copper. As with the Ag 3d spectra, they were substantially the same and contained sharp doublet peaks originating from Cu $2p_{3/2}$ and $2p_{1/2}$. While Cu_2O several nm thick is generally found on a copper surface, the difference in the binding energy between the metallic copper and Cu_2O is too small to distinguish in the Cu 2p XPS spectra.[21] The weak, broad satellite peaks, indicated by arrows, correspond to small amounts of cupric species (Cu^{2+}) on the copper surface. While similar satellite peaks were previously observed for an as-cleaned copper surface,[21] in this study the copper surface was sputtered by Ar^+ until carbon and oxygen were not observed in the spectra. Therefore, the initial surface conditions were different. Apparently, cupric species, such as $Cu(OH)_2$, formed during exposure.

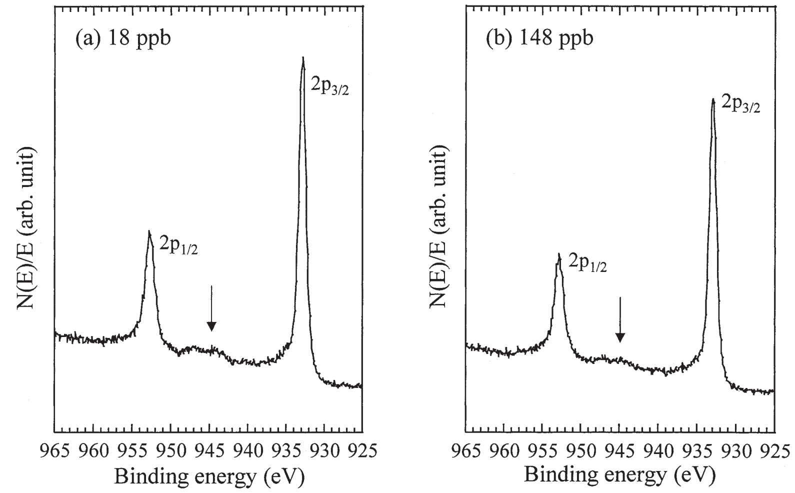

Fig. 4 Cu 2p XPS spectra of copper exposed for one hour to flowing air containing (a) 18 and (b) 148 ppb SO_2.

The Cu 2p XPS spectra of copper exposed to an urban atmosphere in previous studies[21),25] are completely different from those obtained in this study. For comparative purposes, the Cu 2p spectrum of copper exposed to an urban atmosphere is shown in Fig. 5. The broadening of the Cu $2p_{3/2}$ and $2p_{1/2}$ peaks and presence of the satellite peaks due to the generation of cupric species are clearly observed. Phase identification of the copper patinas by X-ray diffraction revealed that Cu_2O and hydrated basic copper sulfate ($Cu_4SO_4(OH)_6 \cdot H_2O$) formed. The latter compound would account for the change in the Cu 2p XPS spectra.

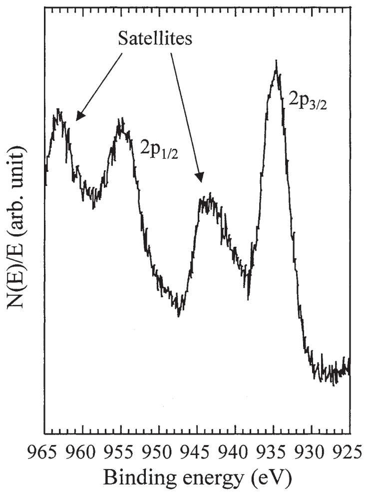

Fig. 5 Cu 2p XPS spectra of copper exposed for one month to an urban atmosphere.

The O 1s XPS spectra for the copper, shown in Fig. 6, are similar to those observed for silver in terms of the

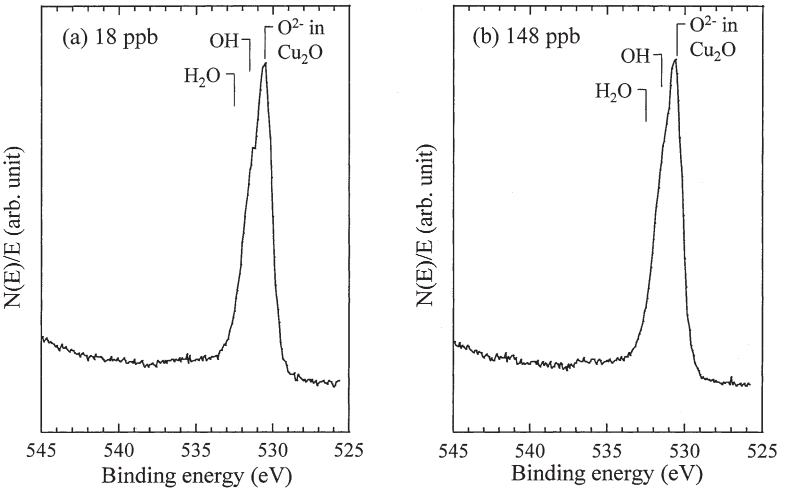

Fig. 6 O 1s XPS spectra of copper exposed for one hour to flowing air containing (a) 18 and (b) 148 ppb SO_2.

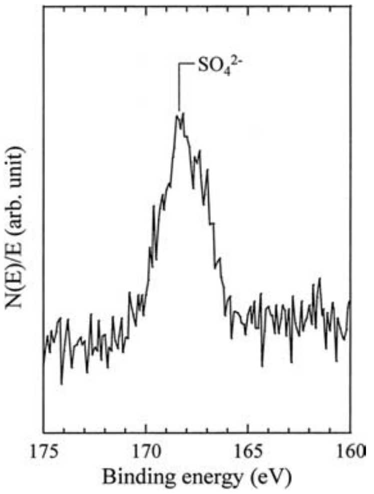

Fig. 8 S 2p XPS spectra of copper exposed for one month to an urban atmosphere.

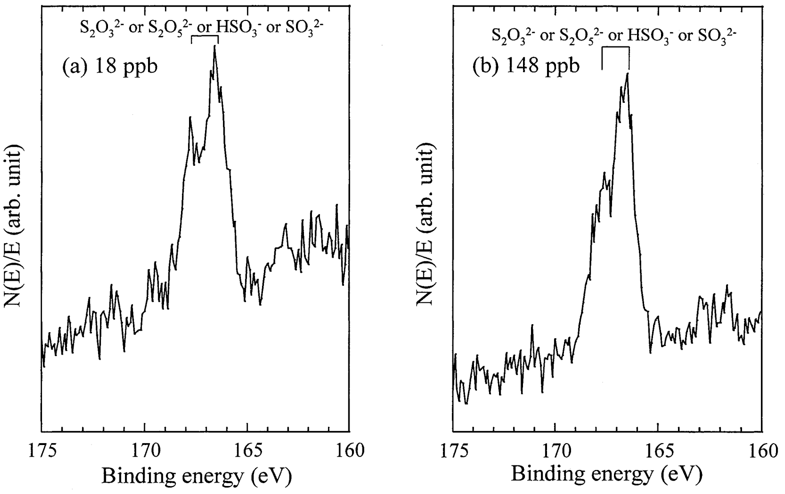

Fig. 7 S 2p XPS spectra of copper exposed for one hour to flowing air containing (a) 18 and (b) 148 ppb SO_2.

binding energy (Fig. 2); however, the peak shape is different. The broadening of the O 1s XPS spectra indicates the presence of another component. There was no obvious difference between the two spectra. As shown in Fig. 6, there were three components in the spectra.[21] The peak at the lowest binding energy (530.5 eV) originated from the O^{2-} in Cu_2O. The presence of O^{2-} in the Cu_2O component indicates Cu_2O formation during exposure. The other two components were oxygen in hydroxyl and oxygen in bound water.

The S 2p XPS spectra for the copper (Fig. 7) differ from those for the silver. The two peaks originated from the $2p_{3/2}$ and $2p_{1/2}$. The difference between the S 2p spectra for silver and copper will be discussed in the next section. Rickett and Payer reported a peak at 166.8 eV in the S 2p XPS spectra of copper exposed to 75 ppb SO_2 for 60 hours.[10] They thought it reasonable that the peak originated from bisulfite; however, some oxy-sulfur ions, such as $S_2O_4^{2-}$ and $S_2O_5^{2-}$, have a binding energy that falls within the same binding energy region.[10] As shown in Fig. 7, the binding energies of $2p_{3/2}$ were 166.6 and 166.5 eV for copper exposed to flowing air containing 18 and 148 ppb SO_2, respectively. These binding energies agree well with the ones from bisulfite or sulfite, as shown in Table 1. Although oxy-sulfur ions cannot be ruled out, it is possible to observe a peak originating from bisulfite, which is generated when SO_2 dissolves into the surface electrolyte.

It is important to note that the S 2p XPS spectra for the copper (Fig. 7) differed from those for copper exposed to an urban atmosphere, an example of which is shown in Fig. 8 for comparison. There is one peak centered at around 168.5 eV.[21), 25] Its broadness indicates that there is one more component on the lower binding energy side, but its contribution is negligibly small. The peak centered at 168.5 eV can be assigned to sulfate, which mainly originated from the hydrated basic copper sulfate ($Cu_4SO_4(OH)_6 \cdot H_2O$) that had formed.[21),25] In the urban atmosphere, both SO_2 and particulate sulfate adsorbed on and dissolved into the surface electrolyte on the copper surface. The former easily oxidized into stable sulfate ions due to the presence of oxidizing agents such as OH radicals (OH·) and hydrogen peroxide (H_2O_2). As a result, sulfate is the main component observed in the S 2p XPS spectra.

3.3 Difference in chemical state

The difference in the chemical state of the sulfur between silver and copper exposed to a low SO_2 concentration for one hour was also examined. Fig. 9 shows the S 2p XPS spectra for the silver (Fig. 3(a)) and the copper (Fig. 7(a)) again for comparative purposes. As described above, there is a significant difference between the two spectra. That is, three components were observed in the S 2p XPS

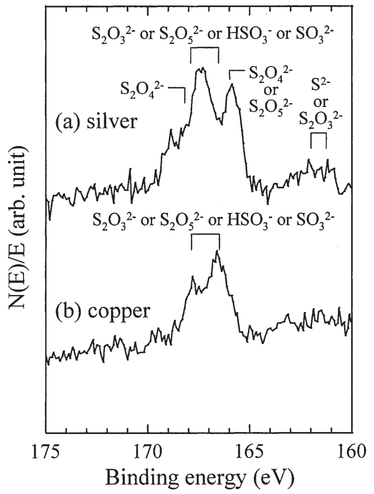

Fig. 9 S 2p XPS spectra of (a) silver and (b) copper exposed for one hour to flowing air containing 18 ppb SO_2.

spectra for the silver, while only one was observed in that for the copper.

When SO_2 adsorbs on the surface electrolyte, the dissolution can be described as

$$SO_2 + H_2O \rightarrow H^+ + HSO_3^- \qquad (1)$$

The bisulfite ions further dissolve into protons and sulfite ions when the pH of the surface electrolyte is high.

$$HSO_3^- \rightarrow H^+ + SO_3^{2-} \qquad (2)$$

In the final stage, sulfite ions are oxidized by the dissolved oxygen in the surface electrolyte, resulting in the formation of stable sulfate ions.

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \qquad (3)$$

This reaction is also promoted by other oxidizing agents. For copper exposed to an atmospheric environment, the resulting sulfate contributes to the formation of basic copper sulfates such as $Cu_4SO_4(OH)_6 \cdot H_2O$ and $Cu_4SO_4(OH)_6$.[26] However, the reaction described by equation (3) apparently did not occur in our study as we did not observe the sulfate component in the S 2p XPS spectra. This is possibly because the exposure time was too short for the sulfite to oxidize.

For silver, the three observed peaks may have arisen from bisulfite, $S_2O_5^{2-}$, $S_2O_3^{2-}$, and/or S^{2-}. If the exposure time is lengthened, the sulfide ions react with the metallic silver and form silver sulfide (Ag_2S). Franey et al. demonstrated that the rate of silver sulfidation by SO_2 is more than two orders of magnitude lower than that by reduced sulfur, such as H_2S and COS.[12] However, the S 2p spectra we obtained for the silver suggests that the contribution of SO_2 to silver sulfidation is significant if, as we assume, the broad peak at around 162 eV is mainly due to the sulfide. It is well known that Ag_2S is a thermodynamically stable phase and that silver does not form sulfate under ordinary conditions.[22] McLeod and Rogers reported that SO_2 in the atmosphere easily dissolves into the surface electrolyte and that the resulting sulfurous acid (H_2SO_3) can act either as a reducing agent or an oxidizing one.[27] We believe that there is a reduction route of bisulfite ions as follows.

$$HSO_3^{2-} \rightarrow S_2O_5^{2-} \rightarrow S_2O_3^{2-} \rightarrow S^{2-} \qquad (4)$$

For copper, the bisulfite seen in the S 2p XPS spectra originated from SO_2 adsorption on the surface electrolyte, as shown in equation (1). Although Chawla and Payer reported the formation of copper sulfide (Cu_2S) in the early stage of copper corrosion with 0.5% SO_2,[28] we did not detect any sulfide component (Fig. 9(b)). Our results agree well with those reported by Rickett and Payer.[10] It is interesting that there was a difference in the chemical state of sulfur between silver and copper exposed to the same atmosphere. The difference was due to the formation of native oxide; that is, the former did not form a stable oxide while the latter immediately formed Cu_2O as soon as it was exposed to air. This Cu_2O on copper may impede the reduction of bisulfite or other oxy-sulfur ions. Rozenfeld proposed the following reduction mechanism.[29]

$$H_2O + SO_2 \rightarrow H_2SO_3 \qquad (5)$$

$$2H_2SO_3 + H^+ + 2e^- \rightarrow HS_2O_4^- + 2H_2O \qquad (6)$$

$$HS_2O_4^- + 7H^+ + 10e^- \rightarrow 2S^{2-} + 4H_2O \qquad (7)$$

The protons represented in equations (6) and (7) may have dissolved the Cu_2O as follows.

$$Cu_2O + 2H^+ \rightarrow 2Cu^+ + H_2O \qquad (8)$$

The protons also dissolved the cupric species identified in the Cu 2p XPS spectra. As a result, reduction species did not form on the copper. Although we have demonstrated a clear difference between silver and copper when they are exposed to flowing air containing SO_2, more detailed studies are needed to clarify the cause.

4. Conclusion

Chemical state analyses of silver and copper plates exposed for one hour to flowing air containing 18 and 148 ppb SO_2 were carried out using XPS to get a better understanding of the initial corrosion behavior of these two metals. The findings are summarized as follows.

1) There was no difference in the shape of the XPS spectra between the two SO_2 concentrations. This indicates that the chemical state of the elements, including the base metals (silver and copper), oxygen, and sulfur does not depend on the SO_2 concentration. The Ag 3d spectra revealed that the silver still had its metallic characteristics even after exposure whereas the copper oxidized during exposure, forming Cu_2O and cupric species such as $Cu(OH)_2$.

2) The S 2p XPS spectra for the silver revealed three peaks originating from bisulfite, $S_2O_5^{2-}$, $S_2O_3^{2-}$, and/or S^{2-}. The bisulfite originated from the dissolution of SO_2 into the surface electrolyte, while the $S_2O_5^{2-}$, $S_2O_3^{2-}$, and S^{2-} originated from the reduction of sulfurous acid. The S^{2-} possibly formed silver sulfide. In contrast, only bisulfite was observed in the S 2p spectra for the copper. It also originated from the SO_2 dissolution. The difference in the chemical state of sulfur between the silver and copper is attributed to the presence of native oxide on the surface,

which may impede the reduction of bisulfite.

References

1) M. Watanabe, A. Hokazono, T. Handa, T. Ichino, and N. Kuwaki, *Corros. Sci.*, **48**, 3759 (2006).
2) W. H. Abbott, *Br. Corros. J.*, **24**, 153 (1999).
3) P. Eriksson, L-G. Johansson, and H. Strandberg, *J. Electrochem. Soc.*, **140**, 53 (1993).
4) J. Tidblad and C. Leygraf, *J. Electrochem. Soc.*, **142**, 749 (1995).
5) M. Lenglet, J. Lopitaux, C. Leygraf, I. Odnevall, M. Carballeira, J-C. Noualhaguet, J. Guinement, J. Gautier, and J. Boissel, *J. Electrochem. Soc.*, **142**, 3690 (1995).
6) H. Strandberg and L-G. Johansson, *J. Electrochem. Soc.*, **144**, 81 (1997).
7) S. P. Sharma, *J. Electrochem. Soc.*, **127**, 21 (1980).
8) T. E. Graedel, J. P. Franey, G. W. Kammlott, and J. M. Vandenberg, *J. Electrochem. Soc.*, **134** 1632 (1987).
9) Z. Peide, R. P. M. Procter, W. A. Grant, and V. Ashworth, *Nucl. Instrum. Methods*, **209/210**, 841 (1983).
10) B. I. Rickett and J. H. Payer, *J. Electrochem. Soc.*, **142**, 3713 (1995).
11) B. I. Rickett and J. H. Payer, *J. Electrochem. Soc.*, **142**, 3723 (1995).
12) J. P. Franey, G. W. Kammlott, and T. E. Graedel, *Corros. Sci.*, **25**, 133 (1985).
13) L. Volpe and P. J. Peterson, *Corros. Sci.*, **29**, 1179 (1989).
14) D. W. Rice, P. Peterson, E. G. Rigby, P. B. P. Phipps, R. J. Cappell, and R. Tremoureux, *J. Electrochem. Soc.*, **128**, 275 (1981).
15) T. E. Graedel, J. P. Franey, G. J. Gualtieri, G. W. Kammlott, and D. L. Malm, *Corros. Sci.*, **25**, 1163 (1985).
16) D. Persson and C. Leygraf, *J. Electrochem. Soc.*, **142**, 1459 (1995).
17) J. Itoh, T. Sasaki, M. Seo, and T. Ishikawa, *Corros. Sci.*, **39**, 193 (1997).
18) J. Itoh, T. Sasaki, and T. Ohtsuka, *Corros. Sci.*, **42**, 1539 (2000).
19) E. Toyoda, M. Watanabe, M. Suzuki, H. Ando, Y. Higashi, T. Tanaka, M. Matsumoto, T. Ichino, and Y. Miyata, *Zairyo-to-Kankyo*, **54**, 31 (2005).
20) J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, "Handbook of X-ray Photoelectron Spectroscopy", Perkin-Elmer Corporation, Physical Electronics Division (1992).
21) M. Watanabe, M. Tomita, and T. Ichino, *J. Electrochem. Soc.*, **148**, B522 (2001).
22) T. E. Graedel, *J. Electrochem. Soc.*, **139**, 1963 (1992).
23) H. Kim and J. H. Payer, *The Journal of Corrosion Science and Engineering*, **1**, Paper 14 (1999).
24) H. Sekiyama, N. Kosugi, H. Kuroda, and T. Ohta, *Bull. Chem. Soc. Jpn.*, **59**, 575 (1986).
25) M. Watanabe, Y. Higashi, and T. Ichino, Paper 045 presented at 15th International Corrosion Congress, Granada, Spain (2002).
26) M. Watanabe, E. Toyoda, T. Handa, T. Ichino, N. Kuwaki, Y. Higashi, and T. Tanaka, *Corros. Sci.*, **49**, 766 (2007).
27) W. McLeod and R. R. Rogers, *Corrosion*, **22**, 143 (1966).
28) S. K. Chawla and J. H. Payer, *J. Electrochem. Soc.*, **137**, 60 (1990).
29) I. L. Rozenfeld, "Atmospheric Corrosion of Metals", E. C. Greco, Editor, p.125, NACE, Houston, Texas (1972).

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要　　旨

二酸化硫黄は金属の大気腐食に影響を与える典型的なガスである．銀及び銅の大気腐食に及ぼす二酸化硫黄の影響についてはこれまで多くの研究がなされてきたが，初期腐食挙動についてはほとんど知見が得られていない．本研究ではX線光電子分光（XPS）により低濃度二酸化硫黄（18及び148 ppb）を含む大気に暴露した銀及び銅板上の硫黄の化学状態を分析した．いずれの二酸化硫黄濃度においてもXPSスペクトルの形状は同一であり，元素の化学状態は二酸化硫黄濃度に依存しないことを示していた．また，銀板上と銅板上の硫黄の化学状態は異なることを見い出した．銀の場合には，bisulfite，$S_2O_5^{2-}$, $S_2O_3^{2-}$, S^{2-}に由来する3つのピークが観測された．bisulfiteは表面吸着水への二酸化硫黄の溶解に，その他の成分は亜硫酸の還元に由来するものと考えられる．一方，銅の場合にはbisulfiteに由来する成分のみが観測された．この成分も表面吸着水への二酸化硫黄の溶解に由来する．銀板上と銅板上に存在する硫黄の化学状態の差異は，bisulfiteの還元を妨害すると思われる酸化物の存在に起因する．

キーワード　銀，銅，大気腐食，二酸化硫黄，X線光電子分光（XPS），化学状態分析