Characterization of surface carbon films on weathered Japanese roof tiles by soft x-ray spectroscopy

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The effects of weathering on carbon films deposited on Japanese smoked roof tiles were investigated by soft x-ray absorption and emission spectroscopy using synchrotron radiation. X-ray absorption measurements revealed that weathering oxidizes the carbon films and that partial carboxy chemical bonding occurs. Incident angle-dependent x-ray absorption spectra in the C K region confirmed that the degree of the orientation at the surface of the oxidized carbon films decreases with weathering. However, the take-off angle-dependent C K x-ray emission spectra showed that the orientation of the layered carbon structure is maintained in the bulk portion when weathered. Therefore, it is confirmed that oxidation proceeds from the surface of the carbon films. Weathering degrades and oxidizes the surface carbon films, which causes the metallic silver color to change to darker gray. Copyright © 2005 John Wiley & Sons, Ltd.

INTRODUCTION

The Japanese smoked roof tile ‘Ibushi-Kawara’ (hereafter referred to as Kawara or tile) is made from a sintered clay plate with a carbon film coating on the surface. The outstanding features of Kawara include the metallic silver color and weather resistance, which essentially originate from the surface carbon films deposited by chemical vapor deposition (CVD) of hydrocarbons. To understand the features from a chemical-bonding viewpoint, Motoyama et al.1 characterized the carbon films using electron probe microanalysis (EPMA), small-angle x-ray scattering and transmission electron microscopy (TEM), which revealed that the carbon films consisted of plane, spherical and fibrous carbons. To understand further the carbon films on Kawara, we recently investigated them by soft x-ray absorption and emission spectroscopy using synchrotron radiation. Our previous study2 revealed that the carbon films consist essentially of carbon black-like sp2 carbon atoms that have a unique microstructure. Half of the carbon atoms form layered clusters parallel to the basal clay plane, which results in the metallic color, and the remaining half form random clusters, which connect the layered clusters rigidly and result in durability. The degraded carbon films, on which black stripes occasionally form during the smoking process, have also been investigated3 and it was revealed that the degraded carbon films contain more random clusters than layered clusters. These studies demonstrated that soft x-ray absorption and emission spectroscopy using synchrotron radiation are powerful tools for analyzing the chemical bonding of the carbon films and for evaluating the quality of Kawara.

In this study, we further investigated the carbon films to understand the weathering effects on Kawara. The outstanding weathering effect involves a change of color, in which the typical metallic silver color of fresh Kawara changes to a darker gray during long-term weathering on roofs. Therefore, we measured the soft x-ray absorption and emission spectra of weathered Kawara in order to investigate the change of color from a chemical-bonding point of view.

EXPERIMENTAL

Five pieces of Kawara, which were individually made in 1994, 1997, 1999, 2000 and 2002, were weathered until 2002, i.e. the five tiles were weathered for 8, 5, 3, 2 and 0 years, respectively. Figure 1 shows photographs of the sample pieces of the weathered Kawara used for spectroscopic measurements. The unweathered Kawara-2002 displays a metallic silver color. However, as the weathering period increased, the Kawara turned a darker gray. Spectroscopic measurements of the soft x-ray absorption and emission were performed at the beamlines BL-6.3.24 and BL-8.0.1,5 respectively, at the Advanced Light Source (ALS). In BL-6.3.2, total electron yield (TEY) x-ray absorption spectra were measured by monitoring the sample photocurrent using 600 or 1200 lines mm−1 gratings with a 50 μm exit slit. The 1200 lines mm−1 grating was used for wide-range scanning up to 1000 eV and the 600 lines mm−1 grating for...
short-range-scanning in the C K and O K regions. Chemical-bonding information on the target surface was obtained by surface-sensitive TEY x-ray absorption measurements. In BL-8.0.1, C K x-ray emission spectra were measured using a grating x-ray spectrometer equipped with a 600 lines mm\(^{-1}\) grating and a 50 µm entrance slit. The photon energy of the monochromatized incident beams was tuned to 320 eV. Chemical-bonding information on the bulk portion in target materials was obtained by bulk-sensitive x-ray emission spectroscopy. In both BL-6.3.2 and BL-8.0.1, the electric field vectors of the incident synchrotron radiation beams were in the horizontal plane. Therefore, the sample pieces were rotated around the vertical axis to evaluate quantitatively the orientation of the sp\(^2\) carbon atoms in the carbon films on the weathered Kawara from the incident/take-off angle-dependent soft x-ray absorption and emission spectra.\(^6\)

**RESULTS AND DISCUSSION**

Figure 2 shows the TEY x-ray absorption spectra scanned in the wide-energy range (190–1100 eV) of the weathered Kawara and HOPG, which were measured with a 90° incident angle (normal incidence). The x-ray absorption peaks of C K, O K (first and second orders), Ca L and Fe L are observed in the Kawara. Other elements such as nitrogen (K 1s absorption edge = 410 eV), sodium (K 1s = 1071 eV) and the transition metals [Ti, V, Cr, Mn, Co, Ni, Cu Zn (whose L 2p absorption edges are in the 560–1044 eV region)] were not observed. Although the peak intensities of Ca L and Fe L clearly seem to be independent of the weathering period, the peak intensity of O K seems to depend on it. Figure 3 shows the TEY x-ray absorption spectra expanded in the 200–600 eV region of Fig. 2. The inset shows the weathering period dependence of the intensity ratios of O K (first and second orders) peaks to the C K peak. Except for the 5-year weathered Kawara, the O K/C K peak intensity ratios are almost proportional to the weathering period. The reason why the 5-year sample may be different is due to a non-uniform weathering effect on the Kawara surface. As shown in Fig. 1, the color of the 5-year weathered sample (Kawara-1997) is not uniform. Therefore, the x-ray absorption spectrum of the 5-year weathered Kawara may have been measured on the less weathered spots on the surface. It is confirmed that weathering oxidizes the carbon films on Kawara.

In order to analyze the chemical bonding of the oxidized carbon films on the weathered Kawara, the x-ray absorption spectral features in the O K region of the Kawara were...
Figure 3. TEY x-ray absorption spectra in the range 200–600 eV of the weathered Kawara. The inset shows the weathering period dependence on the peak intensity ratio of O K/C K in the x-ray absorption edges.

Figure 4. TEY x-ray absorption spectra in the O K region of the weathered Kawara and reference organic compounds that have various oxygenated functional groups. The TEY intensity of the spectra is normalized by the ESC peak intensity. Although the spectral features of the reference carbon black do not display an angle dependence, the peak intensities of the ESC peak in the Kawara and HOPG increase as the incident angle decreases. This angle dependence of the x-ray absorption is explained by the orientation of the layered sp² carbon atoms. Therefore, Fig. 6 indicates that the carbon films on the Kawara partially take a layer structure similar to HOPG. However, the degree of orientation in the carbon films seems to be dependent on the weathering period since the incident angle dependence of the ESC peak intensity clearly depends on the weathering period. To evaluate quantitatively the orientation of the carbon films on the Kawara, the incident angle dependence of the ESC/EM peak intensity ratios of the Kawara and HOPG was plotted and the slopes of the approximated linear functions of the angle dependences are displayed in the insets. The slope is a simple index for the degree of orientation of the surface portion of the carbon films. The steeper the slope, the higher is the orientation. The slopes for the Kawara (the insets) become gentler as the weathering period increases. Therefore, it is determined from the orientation of the carbon films compared with reference organic compounds with various oxygenated functional groups. Figure 5 shows the TEY x-ray absorption spectra in the C K region of the weathered Kawara and the reference compounds. The spectra of the reference compounds confirm that the peak energy of the small peaks at the thresholds depends strongly on the type of oxygenated functional groups. The weathered Kawara displays a small peak at 531 eV, which corresponds approximately to the peak energy of a carboxy group. Therefore, it is concluded that the oxygenated carbon films on the weathered Kawara partially have a carboxy chemical bonding.

films, especially in the surface layer observed by the surface-sensitive TEY x-ray absorption spectroscopy, that weathering degrades Kawara. The degraded orientation is explained by C–C bond breaking in the layered clusters from the oxidation caused by weathering. Figure 7 shows the take-off angle-dependent C K x-ray emission spectra of the weathered Kawara and HOPG. The x-ray intensity of the spectra is normalized by the 277 eV peak intensity. In the spectral features of Kawara and HOPG, the main peak near 277 eV is mostly due to the $\pi^*$ portion of the C 2p density of states and the high-energy shoulder near 282 eV is due to the $\sigma^*$ portion. The relative intensity of the high-energy shoulder ($\pi^*$) clearly depends on the take-off angle and the high-energy shoulder intensity increases as the take-off angle increases for both Kawara and HOPG. This angle dependence of the x-ray emission is well explained by the orientation of the sp$^2$ carbon atoms. Portions of $\pi^*$ and $\sigma^*$ in these spectra can be separated experimentally$^{2-6}$ and the take-off angle dependence of the intensity ratios of the $\pi^*/\sigma^*$ portions are plotted in the insets.

The slopes of the approximated linear functions of the $\pi^*/\sigma^*$ ratios in x-ray absorption spectra, the slopes obtained from the x-ray emission spectra can also be a simple index for the degree of layer orientation for bulk carbon films. The slopes for the weathered Kawara are nearly 0.005°$^{-1}$ and are not dependent on the weathering period. This shows that on Kawara the orientation of the carbon films, especially in the bulk layers as observed by the bulk-sensitive x-ray emission measurements, is not degraded by the weathering. Figure 8 shows the weathering-period dependence of the slopes of the approximated linear functions for the $\pi^*/\sigma^*$ ratio in the incident angle-dependent x-ray absorption and the $\pi^*/\sigma^*$ ratio in the take-off angle-dependent x-ray emission spectra, obtained from Figs 6 and 7, respectively. The slope of the absorption is almost proportional to the weathering period, which shows that the orientation at the surface of the carbon films is degraded by weathering. Further, the slope of
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CONCLUSION

The soft x-ray absorption and emission spectra of weathered Kawara were measured to elucidate weathering effects on the carbon films. From the absorption measurements, it is confirmed that weathering oxidizes the carbon films and that the films have partial carboxy chemical bonding. From the incident/take-off angle dependent x-ray absorption and emission measurements, it is concluded that the carbon films are oxidized from the surface and that the degree of orientation at the surface decreases with oxidation. The change in color from metallic silver to a darker gray results from the degraded and oxidized surface structure due to weathering. However, the orientation of the bulk portion in the carbon films is maintained even after 8 years of weathering. In addition, it is well demonstrated that soft x-ray absorption and emission spectroscopy using synchrotron radiation are powerful tools for analyzing the chemical bonding of CVD carbon films.

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REFERENCES