Nondestructive Measurement of Hexavalent Chromium in Chromate Conversion Coatings using X-ray Absorption Near-Edge Structure

Chromate conversion coatings (CCCs) have been widely used for electrical components and mechanical parts, made of brass, aluminum, copper or galvanized iron, to prevent rust formation at a reasonable cost. CCCs have often contained a hexavalent chromium (Cr^{6+}) in addition to a trivalent chromium (Cr^{3+}). Cr^{6+} is known to be toxic and soluble in water. In contrast, Cr^{3+} is nontoxic and mostly insoluble in water. In connection with RoHS (Restriction of the use of certain Hazardous Substances) regulation [1], components containing Cr^{6+} will not be allowed to be used in the electric and mechanical products. Therefore, it is important to analyze the chemical state of chromium (Cr) and to estimate the concentration of Cr^{6+} in a CCC.

The X-ray absorption near-edge structure (XANES) is known to provide useful information on the chemical bonding state of the materials. Recently, Shaffer *et al.* and Tsuyumoto *et al.* investigated chromium in soil [2] and in Portland cement [3], respectively. In comparison with these bulk materials, a CCC is a thin layer of thickness less than 1 μm. In the following, we describe the development of an evaluation technique for Cr^{6+} in the thin coating layer, including the depth distribution of Cr^{6+}.

For the high-sensitive detection of fluorescent X-rays from CCCs, we used a silicon drift detector (SDD) with seven elements. The measurements were performed at beamline **BL16B2**. In Fig. 1, we show the normalized Cr-K XANES spectra for black, yellow, colored and nonhexavalent CCCs. In the figure, the spectra were normalized by the intensity at 6150 eV where the complex oscillation structure coming from the chemical structure is already smoothed out. The inset shows the pre-edge peak, which is the resonant absorption that corresponds to the 1s to 3*d* transition, which allowed for Cr^{6+} and forbidden for Cr^{3+} [4]. The black, yellow and colored CCCs showed the pre-edge peak that indicates the existence of Cr^{6+} in contrast to the absence of the peak in nonhexavalent CCCs. On the other hand, the fluorescence intensity at the normalization point of 6150 eV, Cr at any valence state, contributes to the fluorescent yield and can be used to estimate the total amount of Cr in a CCC.

To quantify the percentage of Cr^{6+} in a CCC, we used the integrated intensity of the pre-edge peak to minimize the effects from the variation of the spectral shape on the quantification. In the integration, the background was removed by using the profile of the nonhexavalent chromium sample. The percentage of Cr^{6+} can be obtained by multiplying the integrated peak intensity by the calibration constant obtained from the reference sample of CrO_3 as a pure Cr^{6+}.
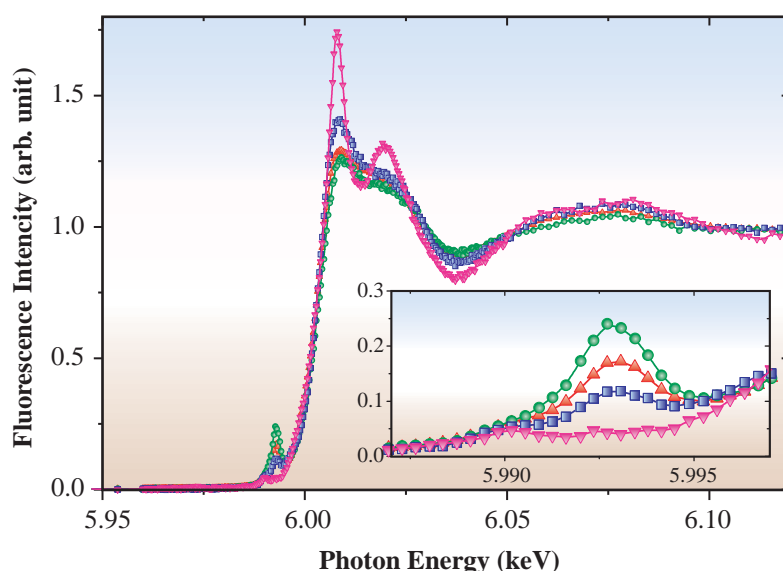

Fig. 1. Normalized Cr-*K* XANES spectra of black ( ), yellow ( ), colored ( ) and nonhexavalent ( ) CCCs. The inset shows an enlarged view of the Cr^{6+} peak area.

This method gives the percentages of Cr^{6+} in the black, yellow, colored and nonhexavalent CCCs, which are 10.5 ± 1.1, 19.3 ± 1.9, 3.5 ± 0.4 and 0%, respectively.

To evaluate the depth distribution of Cr^{6+} in a CCC, we performed grazing incidence X-ray fluorescence (GIXRF) measurements using the wavelength-dispersive detector system at beamline **BL16XU**. We measured the incident angle dependence of the fluorescence yield, which reflects the depth distribution of the element, at 5993 eV and at 6150 eV, which correspond to the pre-edge peak of Cr^{6+} and the total Cr, respectively. The measurement results are shown in Fig. 2(a) where we can see a clear difference in the fluorescent profiles between Cr^{6+} and the total Cr. In the data analysis, we developed an optimization program that is based on the multilayer reflectivity calculation where the fluorescence intensity is calculated from the electric field in the layer and the depth distribution for Cr^{6+} and the total Cr [5]. Since the surface roughness was large, we sliced the CCC into thin layers and the mass density of each layer, which is proportional to the total Cr density, was optimized. Furthermore, the dispersion of the incident angle due to the rough surface was taken into account by assuming the divergence of the incident angle of X-ray to be around 0.1 degree in the calculation. The result of the optimization for the measured X-ray intensity is shown by the solid line in Fig. 2(a). The corresponding depth profile is shown in Fig. 2(b) and the inset figure is the schematic image of Cr^{6+} concentration. The percentage of the Cr^{6+} concentration turned out to decrease along the surface of the yellow CCC. The conventional CCC process includes a water rinse after the formation of a coating. It is possible that the Cr^{6+} around the surface was deoxidized or eluted in the water [6].
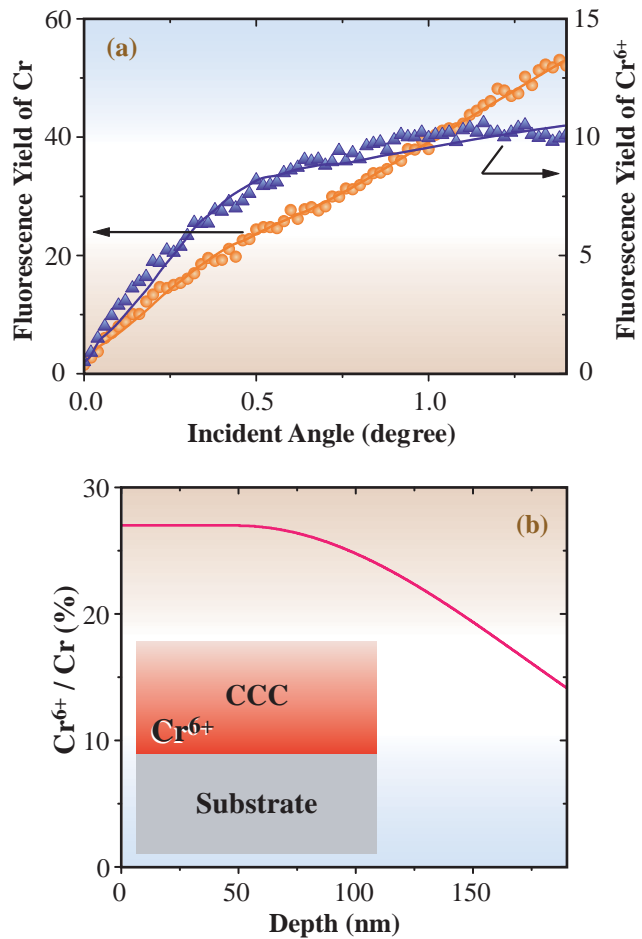

Fig. 2. **(a)** Incident angle dependence of Cr-Kα fluorescence from the total Cr ( ) and at Cr^{6+} pre-edge peak ( ) for yellow CCC. The solid line represents the calculation based on the multilayer model. **(b)** Depth profile of Cr^{6+} ratio. The inset in **(b)** shows a schematic image of Cr^{6+} concentration.

K. Nomura* and N. Awaji

Fujitsu Laboratories LTD.

*E-mail: nomura.kenji@jp.fujitsu.com

References

[1] Official Journal of the European Union **37** (13 February 2003) 19.
[2] R.E. Shaffer *et al.*: Anal. Chim. Acta **442** (2001) 295.
[3] I. Tsuyumoto and H. Uchikawa: J. Ceram. Soc. Jpn. **111** (2003) 608.
[4] S. Bajt *et al.*: Anal. Chem. **65** (1993) 1800.
[5] N. Awaji: Spectrochim. Acta, Part B **59** (2004) 1133.
[6] *K. Nomura and N. Awaji: Jpn. J. Appl. Phys. Lett. **45** (2006) L304.*