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XANES measurements of hexavalent chromium

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Introduction

The chromate conversion coating has been widely carried out to prevent from rust formation of electric component made of galvanized iron, brass or copper. It can provide excellent corrosion protection with low cost. However, chromate solution contains hexavalent chromium (Cr^{6+}) and trivalent chromium (Cr^{3+}). The hexavalent chromium is known to be toxic and soluble in water. On the other hand, the trivalent chromium is nontoxic and mostly insoluble in water. In connection with RoHS (Restriction of the use of certain Hazardous Substances) regulation, it will not be able to use the chromate conversion coating containing the hexavalent chromium in a few years. Therefore, it is important to clarify the chemical state of chromium in chromate conversion coatings and to estimate the quantities of hexavalent chromium. For the purpose, we developed the Cr-K edge XANES measurements for samples containing hexavalent chromium.

Experimental and Results

The XANES experiments were performed at BL-17A. The XANES spectra were measured by the transmission method. As references, samples containing hexavalent chromium (CrO_3, $K_2Cr_2O_7$ and K_2CrO_4) or trivalent chromium (Cr_2O_3 and $Cr(OH)_3 \cdot nH_2O$) were also prepared.

The normalized Cr-K XANES spectra of the reference samples are shown in Fig. 1. Figure 2 shows the area around the hexavalent pre-edge peak. The reference samples containing hexavalent chromium (CrO_3, $K_2Cr_2O_7$ and K_2CrO_4) exhibited the distinct pre-edge peak prior to the main Cr-K absorption edge in contrast to the non appearance in trivalent chromium (Cr_2O_3 and $Cr(OH)_3 \cdot nH_2O$). This pre-edge absorption resonance correspond to the electronic transitions from the 1s core state to the 3d molecular orbital state.

The data analysis of chromate conversion coating is in progress. The Cr^{6+} / Cr in chromate conversion coating can be calculated by using the following equation:

$$Cr^{6+}/Cr = I_{chromate}/I_{reference} \qquad (1)$$

where $I_{chromate}$ and $I_{reference}$ represent intensity of the pre-edge peak for the chromate conversion coatings and the hexavalent reference sample (CrO_3), respectively.

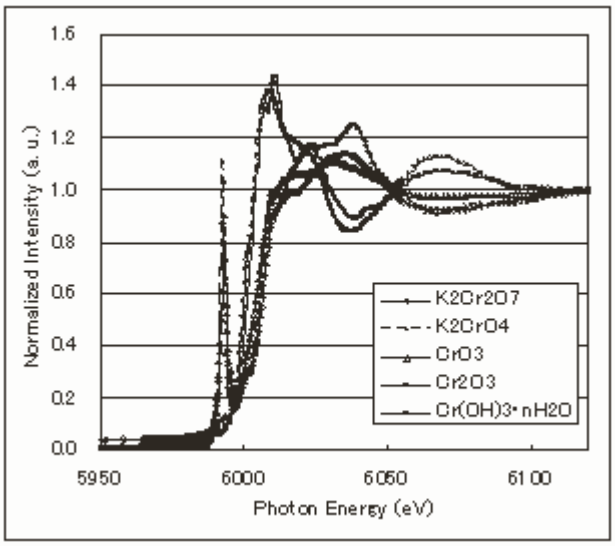

Fig 1. Normalized Cr-K XANES spectra of Cr_2O_3 (◯), CrO_3 (△), $Cr(OH)_3 \cdot nH_2O$ (□), $K_2Cr_2O_7$ (◇) and K_2CrO_4 (×).

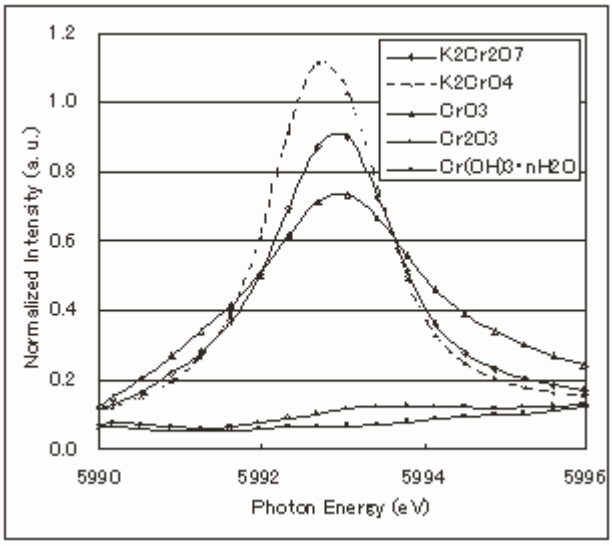

Fig 2. The enlarged figure of the hexavalent pre-edge peak.

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