Microstructure of organic–inorganic composite coatings studied by TEM and XANES

Etsuo Hamada\textsuperscript{a,c,*}, Masayasu Nagoshi\textsuperscript{b}, Kaoru Sato\textsuperscript{b}, Akira Matsuzaki\textsuperscript{a}, Takafumi Yamaji\textsuperscript{b}, Kotaro Kuroda\textsuperscript{c}

\textsuperscript{a}Steel Research Laboratory, JFE Steel Corp., 1 Kokan-cho, Fukuyama, Hiroshima 721-8510, Japan
\textsuperscript{b}Steel Research Laboratory, JFE Steel Corp., 1-1 Minami-watarida-cho, Kawasaki-ku, Kawasaki 210-0855, Japan
\textsuperscript{c}Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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Abstract

Chromate coatings on Zn or Zn alloy coated steel sheets often include silica for the aim to improve corrosion resistance. In the case of dry-in-place chromate coatings containing acrylic resin (hereafter referred to as an organic–inorganic composite coating), an addition of silica, however, did not show an improvement in corrosion resistance. The microstructures of the organic–inorganic composite coatings were observed by transmission electron microscopy (TEM) and the chemical states of Cr were investigated by the total electron yield X-ray absorption near edge structure (TEY-XANES) method. TEM samples were successfully prepared by dry ultramicrotomy preventing water-soluble components in the coatings from dissolving out. TEY-XANES revealed the chemical states of components even in the organic matrix. Using these methods, it was found that the addition of silica changed just the morphology of the chromium compound in the organic–inorganic composite coating but not the chemical state of Cr. This is a reason for the addition of silica being not effective at improving corrosion resistance. The combination of dry ultramicrotomy-TEM and TEY-XANES spectroscopy was proven to be a powerful tool for characterizing organic–inorganic composite coatings.

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1. Introduction

Zn or Zn alloy coated steel sheets are main products of steel industries and are used as corrosion-resistant steels commonly for car bodies, constructs and appliances. These steel sheets are often chromate treated for the improvement of corrosion resistance. Chromate conversion coatings are produced by chemical or electrochemical treatment with mixtures of Cr(VI), Cr(III) and certain other compounds. Since Cr(VI) has a high redox potential, it is reduced to Cr(III) and deposited as hydroxides at scratches or abraded areas (self-healing effect). Protection is due both to the self-healing effect of Cr(VI) in the film and to the physical barrier presented by the film itself [1]. Chromate coatings are categorized into three types by production methods, electrolytic, reacted-in-place and dry-in-place (DIP). Since DIP chromate coating is made simply by application and drying of a chromate solution without rinsing, it has an advantage to the other chromate coatings in point of not discharging waste solution [2]. Basic DIP chromate solution contains Cr(VI), Cr(III) and PO\textsubscript{4}\textsuperscript{3−} and often silica is added to the possible solution for improvement of corrosion resistance. The chemical states of DIP chromate coatings and the role of silica in such coatings have been studied [3–6]. It has been suggested that Cr(VI) adsorbed onto silica is subsequently released and exhibits the self-healing effect when the base metal corrodes [4,5]. Aiming to sustain Cr(VI) more effectively and to improve corrosion resistance, formability and appearance, DIP chromate-organic resin complex coatings (hereafter referred
to as an organic–inorganic composite coating) have been developed [7]. In contrast to inorganic type of DIP chromate coatings, the chemical states of organic–inorganic composite coatings have not been reported. It is likely due to the difficulty of state analysis of a component in an organic matrix. Microstructures of chromate coatings are difficult to investigate as well. Transmission electron microscopy (TEM) is suitable for the observation because the coating thickness is about 10 nm to several μm. However, water-soluble components in chromate coatings easily dissolve out when preparing TEM sample.

In this paper, to get a tip for the coating design, the cross-sectional structures of organic–inorganic composite coatings and the chemical states of Cr are investigated using dry ultramicrotomy—TEM and total electron yield X-ray absorption near edge structure (TEY-XANES) [8]. The relation between corrosion resistance and the presence of silica is discussed.

2. Experimental

Two different chromate solutions were used to treat Zn-55% mass Al alloy coated steel sheets. The first solution was a regular chromate solution containing partially reduced chromic acid, phosphoric acid and acrylic emulsion (10 g Cr/l, Cr(III)/Cr(VI) = 0.43, phosphoric acid/Cr = 1.25, acrylic emulsion/Cr = 75 in weight ratio). The second solution was the same but also contained colloidal silica (SiO₂/Cr = 15 in weight ratio). The resulting sheets were then dried at 393 K. The chromium contents of the deposited layer were about 20 mg/m² of surface. The organic–inorganic composite coatings were bent several parts and were subjected to salt spray test for 240 h according to JIS Z2371.

The cross-sectional microstructures of the organic–inorganic composite coatings were characterized using a thermal field emission gun TEM (Philips CM20 FEG operating at 200 kV) equipped with an energy dispersive X-ray spectrometer (EDS: EDAX Phoenix). TEM specimens were prepared by dry ultramicrotomy to prevent water-soluble components in the coatings from dissolving out. The slices were supported on a Cu grid.

The chemical states of Cr in the organic–inorganic composite coatings were investigated using XANES. Although transmission mode, in which the intensities of incident and transmitted X-ray are monitored, is widely used for XANES measurements, it is not applicable for a substance on a steel sheet. We employed TEY-XANES to solve the problem. TEY-XANES spectrum is obtained by measuring the amount of total electrons emitted as a relaxation process from a sample that absorbs X-ray. In our experiment, the amount of the total electrons was measured by monitoring the specimen current (Fig. 1) [9]. To normalize the specimen current, the intensity of incident X-ray was measured by monitoring the current of a Cu grid located upstream of the specimen. TEY-XANES spectra were measured using synchrotron radiation at KEK-PF BL-27B. As standard samples, Cr(OH)₃, Cr₂O₃, CrPO₄·6H₂O and CrO₃ were used.

3. Results

3.1. Corrosion resistance

After 240 h salt spray test, both the coatings showed a dark corrosion product at bends (1T, 2T, 3T in Fig. 2). The rusted area ratio at bends of the two coatings was 100%, i.e. the two coatings showed the same level of corrosion resistance. This indicates that the corrosion resistance of the organic–inorganic composite coating is not affected by the addition of silica, in contract to that of inorganic DIP chromate coatings.

3.2. Microstructure of the coatings

The regular coating showed a network-like contrast with a diameter of ca. 50 nm in a TEM image (Fig. 3). Electron diffraction of the coating gave neither ring nor net patterns. Cr, O, P, Al and Zn were detected in the network-like dark lines using EDS (Fig. 4(a)). The other peak of Cu in the EDS spectrum results from Cu grid and C; Si are components of acrylic emulsion. Fig. 4(b) shows an EDS spectrum obtained from a bright region enclosed by the network lines, in which just C and Si, components of acrylic emulsion, were detected. This suggests that this region is a resin particle of acrylic emulsion.

In the coating containing colloidal silica, the network-like contrast was not present (Fig. 5). Silica particles cohered and the agglomerations were segregated in the coating (Fig. 5(a)). With major peaks of Si and O, minor peaks of Cr and P arose from the silica agglomerations. A defocused image of the coating showed further spotty contrasts (Fig. 5(b)) apart from those of the silica. From the spotty contrast, Cr, O, P, Al and Zn were detected.
(EDS spectra similar to that shown in Fig. 4(a) were obtained). The spotty contrast was observed throughout the coating.

### 3.3. Chemical state of Cr

Fig. 6 shows Cr K-edge XANES spectra of standard samples. XANES is characterized by two regions. Below a characteristic energy, the absorption edge, relatively little absorption intensity above the base line occurs. As the energy increases above the absorption edge, incident X-rays are strongly absorbed. The absorption edge corresponds to expulsion of a core electron from a bound state to the continuum. This process contrasts with pre-edge transitions, which produce a sharp maximum or peak in absorption. This process is due to electronic transitions from one bound state to another bound state of higher energy. CrO$_3$ has a distinct pre-edge peak characteristic to Cr(VI). The pre-edge peak is due to a transition, which is symmetrically allowed for the non-centrosymmetric tetrahedral coordination found for hexavalent chromium compounds, but is not allowed for octahedral trivalent chromium. The presence of Cr(VI) can be judged by the presence of this pre-edge peak. The other standard samples that consist of Cr(III) present slightly different XANES from each other corresponding to their electronic state. The chemical state of Cr can be distinguished by comparing the fine structures of spectra.

Fig. 7 shows Cr K-edge XANES spectra of the regular coating and the coating containing silica, along with that of the specimen with silica in the coating. The spectrum of the coating with silica shows a distinct pre-edge peak, indicating the presence of Cr(VI). This result is consistent with the EDS analysis, which also showed the presence of Cr(VI) in the coating containing silica.
of CrPO$_4$·6H$_2$O. Both the coatings showed Cr K-edge XANES spectra similar to CrPO$_4$·6H$_2$O, i.e. Cr(III). This indicates that most Cr in the coatings exist as chromium phosphate.

### 4. Discussion

#### 4.1. The regular coating

The TEM observation and the Cr K-edge TEY-XANES spectrum indicate that chromium cation of chromic acid and phosphoric acid anion react to form amorphous chromium phosphate in the regular organic–inorganic composite coating, and that Zn and Al of the substrate surface are oxidized by Cr(VI) and are taken into the coating at the same instant. Thus almost all Cr(VI) is reduced to Cr(III). The amorphous chromium phosphate and the dissolved Zn and Al are distributed over the boundaries of fine resin particles that constitute the matrix of the coating (resin particles of acrylic emulsion adhere to each other and constitute the matrix of the organic–inorganic composite coatings). The microstructure is schematically shown in Fig. 8. This results in the network-like contrast observed in the regular coating.

#### 4.2. The coating containing silica

Similarly in the coating containing silica, most of Cr is present as chromium phosphate (Cr(III)). It is suggested that silica cannot hold Cr(VI) in the organic–inorganic composite coating unlike its behavior in inorganic DIP chromate coatings (as already mentioned, silica adsorb Cr(VI) in inorganic DIP chromate coatings effectively). It seems that the chemical state of Cr in the organic–inorganic composite coating is hardly changed by the addition of silica. This may be a reason for the addition of silica being not effective at improving corrosion resistance. Although the addition of silica changes the morphology of chromium phosphate (schematically shown in Fig. 8), the corrosion resistance is not affected by this change. Although the reason of

![Fig. 4. EDS spectra obtained from (a) the network-like dark line and (b) the bright region enclosed by the network lines.

![Fig. 5. Cross-sectional TEM micrographs of the organic–inorganic composite coating containing silica. (a) The overview and (b) enlarged image. Silica agglomerations and a spotty contrast are indicated by arrows and an asterisk, respectively.](image)
the morphology change is not clear, we suppose that the affinity between the acrylic resin particles and silica may be so strong that the boundaries of the resin particles are occupied by silica and chromium phosphate is localized.

4.3. The characterization methods

In previous studies, X-ray photoelectron spectroscopy (XPS) was mainly used to determine the chemical state of Cr in chromate coatings [4,6], but ion sputtering during specimen cleaning inevitably causes reduction of Cr valency. Also, XPS does not always present the chemical state of bulk. Actually, one type of organic–inorganic composite coating showed no Cr peaks in an XPS spectrum. Because the detected electrons originate from a region at a few hundred nm from the surface [10], TEY-XANES is more suitable for an analysis of organic–inorganic composite coatings that are a few microns in thickness. Infra-red spectroscopy had been used to investigate the chemical state of Cr [2]. However, the absorption by organic resin interferes with the absorption by Cr and makes the attribution difficult. TEY-XANES can reveal the chemical state of a particular component even if the component is in the organic resin matrix.

A focused ion beam (FIB) method is another option for preparing TEM specimens. We successfully prepared TEM specimens of the organic–inorganic composite coatings using FIB and confirmed that the observed microstructures were consistent with those observed when prepared by dry ultramicrotomy. But the specimens are not suitable for EDS analysis due to the steep trench walls surrounding the thin film. Actually, Al and Zn were detected from the resin particles when the TEM samples prepared by FIB were used, although we did not show the EDS spectrum in this

![Diagram](image1)

**Fig. 6.** Cr K-edge TEY-XANES spectra of Cr(OH)₃, Cr₂O₃, CrPO₄·6H₂O and CrO₃.

![Diagram](image2)

**Fig. 7.** Cr K-edge TEY-XANES spectra of CrPO₄·6H₂O, the regular organic–inorganic composite coating and the coating containing silica.

![Diagram](image3)

**Fig. 8.** Schematic figures of the regular organic–inorganic composite coating and the coating containing silica. Al, Zn and silica in the coatings are omitted.
paper. This is due to spurious X-rays from Zn–Al alloy substrate, because Al and Zn were not detected when the TEM samples prepared by ultramicrotomy were used as described in this study. Recently a micro-sampling method in FIB has been developed [11]. Although the micro-sampling method gives a TEM sample suitable for EDS analysis, dry ultramicrotomy is better than the micro-sampling method as far as EDS analysis is concerned, because even the micro-sampling method can cause the redeposition of sputtered materials, that disturbs EDS analysis.

The combination of dry ultramicrotomy and TEY-XANES spectroscopy is proven to be a powerful tool for characterizing the organic–inorganic composite coatings. These methods will also be useful for studying a variety of other organic–inorganic composite coatings.

5. Conclusion

1. The regular organic–inorganic composite coating. Chromic acid and phosphoric acid react to form amorphous chromium phosphate. Thus almost all Cr is reduced to Cr(III). The chromium phosphate is distributed over the boundaries of the fine resin particles that constitute the matrix of the coating film.

2. The coating containing silica. Silica cannot hold Cr(VI) in the organic–inorganic composite coating unlike its behavior in inorganic DIP chromate coatings but changes the morphology of chromium phosphate. The corrosion resistance of the organic–inorganic composite coating is not affected by the change in morphology of chromium phosphate.

3. The characterization methods. TEM samples can be prepared by dry ultramicrotomy preventing water-soluble components from dissolving out. TEY-XANES reveals the chemical states of components in organic–inorganic composite coatings. The combination of dry ultramicrotomy and TEY-XANES spectroscopy is useful to characterize organic–inorganic composite coatings.

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