

Characterization of Organic-Inorganic Composite Thin Films by TEM and XANES

Etsuo Hamada*,^{*1}, Masayasu Nagoshi*, Kaoru Sato*, Akira Matsuzaki*, Takafumi Yamaji*
and Kotaro Kuroda*^{*1}

*Steel Research Laboratory, JFE Steel Corp., 1 Kokan-cho Fukuyama 721-8510 Japan

Fax: 81-84-945-4059, e-mail: e-hamada@jfe-steel.co.jp

^{*1}Department of Materials Science and Engineering, Nagoya University, Nagoya 464-8603 Japan

Fax: 81-52-789-5035, e-mail: kuroda@numse.nagoya-u.ac.jp

Zn or Zn alloy coated steel sheets are often chromate treated for the aim to improve corrosion resistance. Dry-in-place (DIP) chromate coatings containing resin, i.e. organic composite coatings, are organic-inorganic composite thin films. It is well known that an addition of silica to inorganic DIP chromate coatings improves corrosion resistance. In the case of organic composite coatings, an addition of silica, however, did not show an improvement in corrosion resistance. The microstructures of the organic 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. It was found that the chemical state of Cr in the organic composite coating was not changed by the addition of silica and that the corrosion resistance was not affected by the morphology of the chromium compound. The TEM samples were successfully prepared by dry-ultramicrotomy preventing water-soluble components from dissolving out. TEY-XANES revealed the chemical states of components in the organic composite coatings. The combination of dry ultramicrotome TEM and TEY-XANES spectroscopy was proven to be a powerful tool for characterizing the organic-inorganic composite thin films.

Key words: Organic composite coating, Dry ultramicrotomy, Transmission electron microscopy, Total electron yield x-ray absorption near edge structure, Silica, Corrosion resistance

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 aim to improve corrosion resistance. Chromate conversion coatings are produced by chemical or electro-chemical 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 (RIP) 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_4^{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, i.e. organic composite coatings have been developed [7]. In contrast to inorganic type of DIP chromate coatings, the chemical states of organic 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 report, the cross-sectional structures of organic composite coatings (organic-inorganic composite thin films) and the chemical states of Cr in the coatings 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 ($\text{SiO}_2/\text{Cr}=15$ in weight ratio). The resulting sheets were then dried at 393 K. The chromium contents of the deposited layer were about 20 mg/m^2 of surface. The organic 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 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 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 [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.

3. RESULTS

3.1 Corrosion resistance

After 240 h salt spray test, both the coatings showed a dark corrosion product at bends. 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 composite coating is not affected by the addition of silica, in contrast 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. 1). Electron diffraction of the coating gave no ring nor net patterns. Cr, O, P, Al and Zn were detected in the network-like dark lines using EDS. 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. 2 (a)). Silica particles cohered and the agglomerations were segregated in the coating. 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. 2 (b)) apart from those of the silica. From the spotty contrast, Cr, O, P, Al and Zn were detected. The spotty contrast was observed throughout the coating.

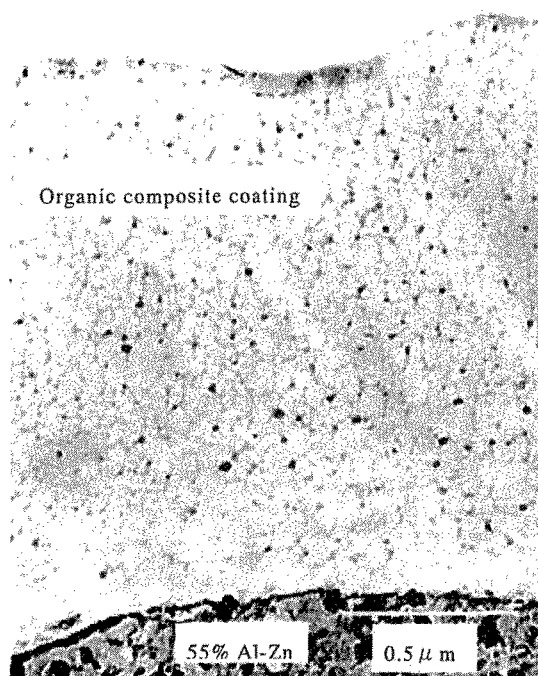


Fig.1 Cross sectional TEM image of the regular coating

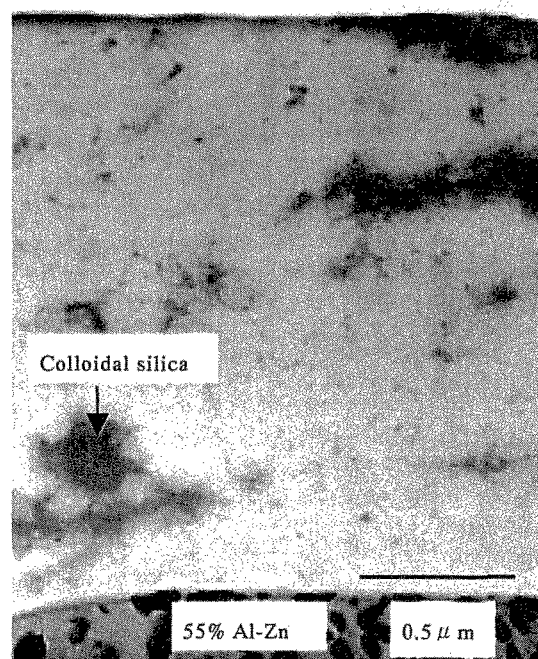


Fig. 2 (a) Cross sectional TEM image of the coating containing silica

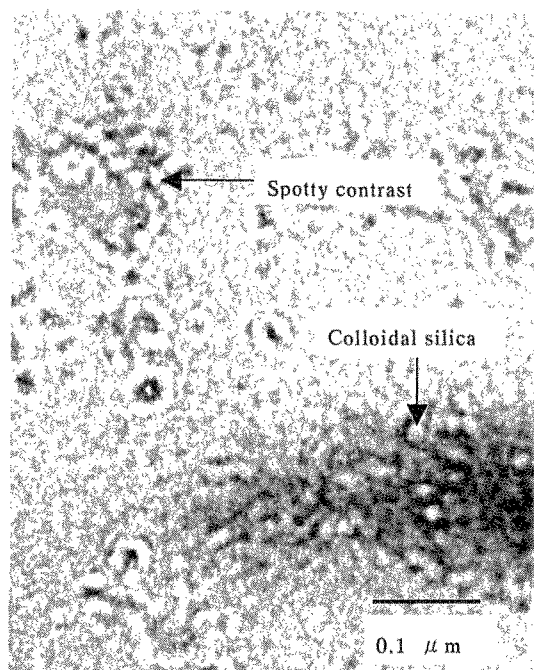
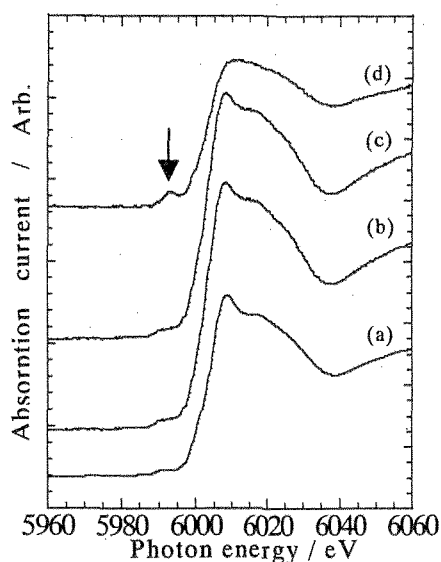


Fig. 2 (b) Enlarged image of fig. 2 (a) to enhance the contrast between the different objects

3.3 Chemical state of Cr

Fig. 3 shows Cr K-edge XANES spectra of the regular coating and the coating containing silica, along with that of $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$. Both the coatings showed Cr K-edge XANES spectra similar to $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$, i.e. Cr(III). This indicates that most Cr in the coatings exist as chromium phosphate. An XANES spectrum of the



coating containing Cr(VI) is also shown in fig. 3 for comparison.

Fig. 3 TEY-XANES spectra of Cr K edge:

(a) $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$ reagent, (b) the regular coating, (c) the coating containing silica, (d) a coating containing Cr(VI). Cr(VI) presents a characteristic pre-edge peak (arrowed).

4. DISCUSSION

4.1 The regular coating

The TEM observation and the Cr K edge TEY-XANES spectrum indicate that chromic acid and phosphoric acid react to form amorphous chromium phosphate in the regular organic 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 composite coatings). 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 can not hold Cr(VI) in the organic 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 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, the corrosion resistance is not affected by this change. Although the reason of 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, 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 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 composite coatings that are a few microns in thickness. Infra-red spectroscopy (IRS) had been used to investigate the chemical state of Cr. 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 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. This is due to spurious x-rays from Zn-Al alloy substrate. 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.

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

5. CONCLUSION

(1) The regular organic 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 loses the ability to sustain a Cr(VI) presence in the coating but changes the morphology of chromium phosphate. The corrosion resistance of the organic 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 composite coatings. The combination of dry ultramicrotomy and TEY-XANES spectroscopy is useful to characterize organic-inorganic composite thin films.

References

- [1] L. F. Spencer, *Metal Finishing*, **58**, 58-63 (1960).
- [2] A. Suda, T. Ogino and S. Tanaka, *Tetsu-to-Hagane*, **7**, 1042-1049 (1991).
- [3] A. Suda, J. Kawaguchi and M. Ogino, *Hyomengijutu*, **46**, 265-269 (1995).
- [4] A. Suda, J. Kawaguchi and M. Ogino, *Hyomengijutu*, **46**, 437-441 (1995).
- [5] A. Suda, J. Kawaguchi and M. Ogino, *Hyomengijutu*, **47**, 183-188 (1996).
- [6] M. Nakazawa and M. Yoneno, *Tetsu to Hagane*, **77**, 115-122 (1991).
- [7] A. Matsuzaki, T. Yamaji and M. Yamashita, *Galvatech 2001*, 663-669 (2001).
- [8] R.G. Jones and D.P. Woodruff, *Surf. Sci.*, **114**, 38-46 (1982).
- [9] A. Erbil, G.S. Cargill III, R. Frahm and R.F. Boehme, *Phys. Rev.*, **B37**, 2450-2564 (1988).
- [10] N. Okude, H. Noro, M. Nagoshi, H. Yamamoto, Y. Baba and T.A. Sasaki, *J. Electron Spectrosc. Relat. Phenom.*, **88-91**, 467-471 (1998).
- [11] H. Koike, T. Ohnishi, T. Ishitani, K. Umemura, S. Tomimatsu and T. Ueno, *Proc. Bunsekidenshikenbikyoku-touronkai*, **15**, 37 (1999).

(Received October 13, 2003; Accepted November 28, 2003)