# Technical Report

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# Structure Analysis of Corrosion Products Using Synchrotron Radiation-Photoemission Spectroscopy and X-ray Fluorescence/Infrared Microspectroscopy

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## Abstract

Regarding photoemission spectroscopy, surface sensitivity is higher than that in previous methods such as XPS or FT-IR by using synchrotron radiation having superior characteristics such as high brightness, energy selectivity or parallel nature as an excitation source in the soft X-ray region. In addition, in X-ray fluorescence / infrared microspectroscopy, an elementary composition and identification of the molecular structure in the film surface, as well as two-dimensional mapping analysis are possible. The depth direction / 2-dimensional distribution of an elementary composition and the molecular structure in corrosion products on a Zn-based coating steel sheet or near Zn-based coating / steel sheet interface were measured by utilizing these analysis technologies.

#### 1. Introduction

In the corrosion reaction of Zn-based coated steel, the corrosion products of Zn have the function of protecting coating film, and the coating film structure, electric conductivity, thermo-dynamic stability, denseness, coating film uniformity etc. are considered to exert influence on cathodic or anodic reactions. Regarding the characteristics and the formation mechanism of corrosion products formed on Zn-based coated steel sheets, several reports have been issued 1-3), and types and compositions of corrosion products of coating film have been analyzed using X-ray diffraction (XRD)<sup>4, 5)</sup>, X-ray photoemission spectroscopy (XPS)<sup>5)</sup>, Raman spectroscopy<sup>6)</sup> and infrared absorption spectroscopy (FT-IR)7). However, in these analysis methods, as the detection depth exceeds several nanometers, it is difficult to distinguish the information about the surface layer and the deep part of corrosion products, or to distinguish the information about the corrosion products formed on a metal in the initial stage of corroding and about the base metal (Fig. 1). However, to clarify the corrosion reaction mechanism in Zn-coating, it is important to clarify the structure of the surface layer of several nanometers right below the surface exposed to a corrosive environment.

In Japan, a number of world-leading synchrotron radiation facilities such as Spring-8, Photon Factory, New-SUBARU, UV-SOR and HiSOR are under operation, wherein a monochromatic radiation of a wave length arbitrarily selected from the series of continuous radiation ranging from the far infrared radiation region to the hard X-ray region is extracted by an enclosed radiation source and a spectroscope, and use thereof is possible. The synchrotron radiation with such characteristics unprecedented by conventional radiation sources is utilized in various fields as new research means.

In recent years, in the field of corrosion research, synchrotron radiation is used for the research of the formation mechanism of passivated film and corrosion products. However, in such research, XRD that employs high brightness synchrotron radiation in the hard X-ray region and XAFS (X-ray absorption fine structure) analysis are applied in many cases, but cases of utilizing synchrotron radiation in the vacuum ultra violet - soft X-ray region are scarce. Nevertheless, since synchrotron radiation is the sole radiation source having high brightness and energy selectivity simultaneously in this energy region, we have attempted to clarify the top surface layer structure and the corrosion-suppressing mechanism of the native oxide film or corrosion products formed on a Zn-Al based hot-dip galvanized steel sheet in the initial stage of corrosion using synchrotron radiation-photoemission spectroscopy (SR-PES) that employs high brightness synchrotron radiation in the soft X-ray region as the excitation radiation source.8-11)

Furthermore, although a hot-dip Zn-55%Al coated steel sheet

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Fig. 1 Corrosion reaction of Zn-Al coating in atmosphere and structure analysis of corrosion products<sup>11</sup>)

exhibits excellent corrosion resistance under an actual environment,<sup>12)</sup> it is reported that when an edge portion is exposed to a 5%NaCl solution spraying environment, the corrosion rate of the coating contacting the steel sheet increases.<sup>13)</sup> This phenomenon is explained by a galvanic model assuming the exposed steel at the edge as the cathode.<sup>14)</sup> In addition, based on the composition, structure and the distribution of the corrosion products formed on the electrodes of Zn/Fe and Zn-55%Al/Fe, the corrosion reaction mechanism based on the mass flow developed by the corrosion reaction has been verified.<sup>15)</sup> As for the elemental composition distribution in corrosion products influenced by the cation transfer developed by the corrosion reaction, an X-ray microscope (SEM-EDS) is used, and for the molecular structure and functional group distributions in corrosion products influenced by anion transfer, infrared microspectrometry ( $\mu$ FT-IR) is used. By comparing and studying the analysis results obtained by applying these methods to an identical scope, analysis of the corrosion reaction influenced by mass transfer is conducted.

This article introduces the research activities of our research group as follows. The group conducted SR-PES/XPS analysis of the native oxide film and the corrosion products of about several nm in thickness, both being formed together on a hot-dip Zn-Al-based coating in the initial stage of corroding and conducted structure analysis of the film top layer and corrosion reaction analysis of a hot-dip Zn-Al-based coated steel. This article further introduces the research group's activity of conducting two-dimensional structure analysis of the corrosion products formed on the steel sheet in the neighborhood of a cut-edge-simulating surface of hot-dip/steel sheet using infrared microspectrometry ( $\mu$ FT-IR) and fluorescent X-ray microspectroscopy (µXRF). The activity of conducting depth-direction two-dimensional structure analysis of the corrosion products formed in the neighborhood of hot-dip Zn-55%Al coating/steel sheet interface, and corrosion reaction analysis in the neighborhood of hot-dip Zn-55%Al coating/steel sheet interface are also introduced

# 2. Structure Analysis of Coating Film Top Layer Using Soft X-ray Synchrotron Radiation<sup>11)</sup>

2.1 Photoemission spectroscopy using soft-X ray stereoscopy

Photoemission spectroscopy (PES) is a surface analysis method using the phenomenon whereby a number of electrons excited inside of a sample by synchrotron radiation from outside of the sample are emitted to an ultra-high vacuum from the sample surface (external photoelectric effect) (**Fig. 2**). And, by diffracting the kinetic energy of the photoelectrons emitted from the sample surface, information about the state of electrons inside the sample, in other words, Valence band structure packed with electrons, and/or core level, is obtained. Namely, by using this method, element types that constitute the sample surface and the state of chemical bonding, for example, state of oxidization at the surface, can be clarified.

The detection depth of photoemission spectroscopy is determined by the escape depth of electrons, the distance from the surface, within which the electrons excited inside the sample can be emitted without inelastic scattering. The escape depth can be estimated with the mean free path of electrons that depends on the magnitude of electron kinetic energy.<sup>16)</sup> The kinetic energy of electrons excited inside the sample is approximately understood as the difference between the exciting synchrotron radiation energy and the binding energy of excited electrons. Accordingly, when examining the shallow core level and or the Valence band that exist within the 100 eV binding energy from the Fermi level, and in the case of XPS wherein Al-K $\alpha$  radiation (1487 eV) is used as exciting synchrotron radiation, the kinetic energy of the detected photoelectron emitted to ultra-high vacuum without inelastic scattering is 1387-1487 eV. Information about the 4 nm surface layer is obtained, judging from the mean free path of the electron. Furthermore, when SR-PES with synchrotron radiation of 150 eV is used as the exciting radiation source, the kinetic energy of the detected photoelectron becomes 50-150 eV, and information limited to a depth of about 1 nm below the surface is obtained.

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Fig. 2 Photoemission spectroscopy using soft X-ray synchrotron radiation<sup>11)</sup>

#### 2.2 Top surface structure analysis of corrosion products on hotdip Zn-Al coating

SR-PES and XPS spectra were measured for the native oxide film, and the corrosion products formed on the hot-dip coatings of Zn-0.2%Al, Zn-5%Al and Zn-55%Al by imparting NaCl particles to the native oxide in the initial stage under a wet atmospheric environment. The SR-PES measurement was conducted by the synchrotron radiation facility of the Laboratory of Advanced Science and Technology for Industry, University of Hyogo (New-SUBARU/BL-7B). Further, the XPS facility manufactured by the Vacuum Generators Company (ESCALAB220i) was used for the XPS measurement. A monochrome Al-K $\alpha$  ray (1487 eV) was used as the synchrotron radiation source.

First, SR-PES/XPS spectra of the native oxide film on hot-dip Zn-5%Al coating before corrosion were measured (**Fig. 3**). For the photoemission intensity of the XPS spectrum, a Zn<sub>3p</sub> peak around 89 eV, Al<sub>2p</sub> peak around 75 eV, O<sub>2s</sub> peak around 24 eV, Zn<sub>3d</sub> peak around 10 eV and O<sub>2p</sub> peak around 6eV were recognized, while from the SR-PES spectrum, the Zn<sub>3p</sub> peak intensity was smaller than that of XPS, and contrarily, O<sub>2p</sub> peak intensity was larger than that of XPS. This is attributed not only to the difference in detection depth but also to the difference in the photoionized cross section between those of the O<sub>2p</sub> peak and Zn<sub>3p</sub> peak when 150 eV synchrotron radiation and 1478 eV Al-K $\alpha$  are used as the exciting radiation source (**Fig. 4**).<sup>17</sup>

The photoionized cross section is an indicator showing the efficiency of ionization of atoms by synchrotron radiation, and differs depending on the type of atom, exciting energy of radiation, and the type of electron to be excited, or the type of electron orbit. Therefore, when quantitative analysis to find the composition ratios of constituent elements is conducted based on the intensity ratio of the



Fig. 3 SR-PES and X-ray spectra of native oxide film on hot-dip Zn-5% coating<sup>11</sup>

peak detected in SR-PES/XPS spectra, respective peak intensity must be corrected by the photoionized cross section. The binding energy of peak  $Al_{2p}$  was larger than 73 eV of Al in the metal state, and the binding energy  $Zn_{3p}$  was larger than 86 eV of Zn in the metal state, respectively. Therefore, both Al and Zn exist in the oxide state.<sup>18</sup>

Next, SR-PES/XPS spectra of corrosion products on the coating after corrosion were measured (**Fig. 5**). In XPS, peaks like those of the native oxide film were observed. However, both peaks of  $Al_{2p}$  and  $O_{2s}$  became considerably small, and the composition ratios of Al and O in the film had decreased. As for the  $Zn_{3p}$  peak, compared with the binding energy of 90 eV of the native oxide film, the value



Fig. 4 Photoionized cross section depended on photon energy<sup>12)</sup>



Fig. 5 SR-PES and XPS spectra of corrosion products on hot-dip Zn-5%Al coating<sup>11</sup>)

shifted chemically to 92 eV in corrosion products, and it is assumed that the state of the chemical bond of Zn has changed from oxide to chloride. In SR-PES, likewise the case of XPS,  $Zn_{3p}$  peak binding energy moves from 90 eV of native oxide to 97 eV. However, the amount of chemical shift is larger than in XPS, which means that the mean state of the Zn chemical bond obtained in the top surface 4nm and the state of the chemical bond limited to the top surface 1 nm obtained in SR-PES are different even though they are both chlorides.

This represents the difference in the states of the local presence of O and Cl in the neighborhood of Zn, and is considered to be attributed to the coordinate number of Cl being larger than that of O, and the shorter bonding length between Zn and Cl than that between Zn and O. As for the Al<sub>2n</sub> peak, in addition to a peak around 75 eV as found likewise in the native oxidation film, a new peak was recognized around 81 eV. Furthermore, in the Valence band of 0-20 eV, although recognized in the native oxide film, the O<sub>20</sub> peak noticed in the native oxide film became considerably small, and contrarily, the Cl<sub>3n</sub> peak became newly apparent instead. This shows that, when exposed to a wet atmospheric environment with the adherence of NaCl particles, the structure of the top surface of 1 nm of corrosion products changes from the native oxide film structure consisting of Al and Zn oxides to the structure wherein the oxides and chlorides of Al and Zn coexist under a state of chemical bond under the dominance of chlorides.

Pertaining to the XPS and SR-PES spectra of the native oxide film and corrosion products after baseline correction, spectrum analysis using the curve-fitting method was performed. The Valence bands of 0-20 eV in the native oxide film and corrosion products were separated into three Gaussian- peaks that pertain to O<sub>2-2</sub> Zn<sub>2-4</sub> and Cl<sub>a</sub>. In addition, the core levels of both the native oxide film and corrosion products of 70-100 eV were separated into two Gaussian peaks that denote two electron states corresponding to Al<sub>2n</sub> and Zn<sub>2</sub>. Then, the separated respective integrated peak intensity was standardized by the photoionized cross section.<sup>12</sup> Finally, the Al/Zn presence ratio was sought based on the peak intensities of  $Al_{2n}$  and  $Zn_{2d}$  of which the dependency of the photoionized cross section on exciting energy is similar, and based on the peak intensities of  $\text{Cl}_{3p}$  and  $\text{O}_{2p}$ , the chloride/oxide ratio was investigated. Then, the influence of AI content of the hot-dip Zn-Al coating on the top surface structures of native oxide film and corrosion products was examined (Fig. 6), wherein XPS exhibits the mean film structure of the top surface layer to a depth of 4nm, and SR-PES exhibits the mean film structure of the top surface layer to a depth of 1 nm.

In the surface layer of 4nm of native oxide film, as the Al content of the coating increases, the  $Al_{2p}/(Al_{2p}+Zn_{3p})$  ratio increases from 0.55 to 0.8. However, in the top surface layer of 1 nm, the  $Al_{2p}/(Al_{2p}+Zn_{3p})$  ratio exceeds 0.95 even in Zn-0.2%Al, and the ratio increases regardless of the Zn-Al alloy compositions, wherein Al oxide is dominant. On the other hand, for corrosion products, the film structure varies depending on the Al content of the coating. In the case of Zn-0.2%Al, Al scarcely exists in the top layer of 1 nm, and Zn chloride mostly exists. Contrarily, in the surface layer of 4 nm, oxides of Al and Zn coexist. In the case of Zn-5%Al, although Al chloride occupies most of the top surface layer of 1 nm, in the surface layer of 4 nm, Zn oxide appears. In the case of Zn-55%Al, in the top surface layer of 1 nm, Al chloride is dominant, and in the surface layer of 4 nm, Al oxide becomes dominant.

As described above, pertaining to the native oxide film on hotdip Zn-Al-based coating, and the corrosion products formed on hotdip coating in the initial stage of corrosion under a wet atmospheric environment with NaCl particles existing on the coating surface, the core level and the Valence band that exist within the binding energy range of 100 eV of a sample were investigated. As a result of using XPS and SR-PES wherein the kinetic energy and the escape depth of a detected photoelectron differ, the mean compositions of the surface layer of 4 nm obtained by XPS and the mean compositions of the top surface layer of 1 nm obtained by SR-PES differ, and accordingly, the surface layer of several nanometers of native oxide film and corrosion products bears a graded composition structure. **2.3 Summary** 

By taking advantage of the difference in detection depth of photoemission spectroscopy that relies on excitation synchrotron radiation energy, the result obtained using the synchrotron radiation in



Fig. 6 Structure of native oxide film and corrosion products film depended on Al content of hot-dip Zn-Al coationg<sup>11</sup>)

the most surface-susceptible soft X-ray region (100–200 eV) and the result obtained using the conventional X-ray source (Al-K $\alpha$ : 1487 eV) were compared. As a result thereof, it was verified in a non-destructive manner that the film structure dominant in native oxide film and corrosion products varies in the depth direction.

#### 3. Two-dimensional Structure Analysis of Coating Surface Layer Using X-ray Fluorescence/Infrared Microspectroscopy<sup>19)</sup>

3.1 Depth-direction two-dimensional structure analysis of corrosion products formed in the neighborhood of cut-edge-simulating surface of hot-dip Zn-55% Al coated steel sheet

To clarify the influence of corrosion products on the corrosion reaction based on the depth-direction two-dimensional distribution of corrosion products formed on the cut-edge surface of a hot-dip Zn-based coated steel sheet, a test specimen simulating a cut-edge surface of a hot-dip Zn-55%Al coating/steel sheet was prepared by removing the coating layer of a Zn-55%Al coated steel sheet by grinding, and by partial exposure of the steel sheet. Then, a corrosion test of a series of salt water spray (SST, 35°C, 22h) and drying (60°C, 25%, 2h) was conducted 25 times for 5% NaCl aqueous solution and artificial sea water.<sup>20)</sup>

Next, a specimen after the corrosion test was embedded in epoxy resin at an angle of 5°, and a specimen for the depth-direction two-dimensional structure analysis of the corrosion products formed in the neighborhood of the cut-edge-simulating surface was prepared by mirror polishing. The two-dimensional mapping measurement of the O-H bond was conducted by infrared microspectrometry apparatus ( $\mu$ FT-IR: Nicolet8700/ContinuumXL) manufactured by Thermo Fischer Scientific, and the two-dimensional mapping of elemental composition was conducted by X-ray Fluorescence microspectroscopy apparatus ( $\mu$ XRF: M4-Tornado manufactured by

Bruker Corporation) (Fig. 7).

On the section where the coating layer is removed and the steel sheet is exposed, based on CCD images, remarkable steel sheet corrosion was confirmed in the case of 5%NaCl aqueous solution, while there was less corrosion in the case of artificial sea water (**Fig. 8**)<sup>19</sup>. Furthermore, regardless of the corroding conditions, a large number of O-H bonds exist in the corrosion products formed in the neighborhood of the coating/steel sheet interface. Moreover, as a result of  $\mu$ XRF analysis of the cross section of the exposed steel region for the case of artificial sea water, the presence of the Mg and Ca hydroxide-formed region was confirmed based on the depth-directional cross section distribution (**Fig. 9**). Namely, when artificial sea water is used, regardless of coating compositions, compounds of Mg hydroxide and Ca hydroxide are formed on the steel sheet near the edge, which effectively suppress the corrosion of steel sheets consequently.<sup>20</sup>

#### 3.2 Summary

Using X-ray fluorescent microspectroscopy ( $\mu$ XRF) and infrared microspectrometry ( $\mu$ FT-IR), two-dimensional structure analysis pertaining to corrosion products formed in the neighborhood of the cut-edge-simulating surface of a hot-dip Zn/hot-dip Zn-55%Al steel sheet was conducted, and as a result of comparison, the depth-direction two-dimensional distribution of corrosion products with Mg hydroxide and Ca hydroxide was revealed. This result supports the steel sheet corrosion-suppressing mechanism of artificial sea water.

#### 4. Conclusion

Synchrotron radiation has higher brightness and excellent energy selectivity as compared with the laboratory-based radiation source, and its usefulness as a surface-analyzing method equipped with not only molecule selectivity but also depth selectivity was confirmed. In future, likewise with hard X-ray for bulk analysis, the use of soft

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# Fig. 7 2D mapping measurement of molecular structure using infrared microspectroscopy and elemental composition using X-ray fluorescence microspectroscopy

X-ray combined with other analysis methods for surface analysis is expected to be an important analysis tool for clarifying the structures of surface oxide layers exposed to a corrosive environment.

In addition, infrared microspectrometry ( $\mu$ FT-IR) realizes the measurement of the two-dimensional distribution (spatial resolution: minimum 10 $\mu$ m) of the molecular structure and functional group under the influence of the anion transfer caused by the corrosion reaction. X-ray fluorescent microspectroscopy ( $\mu$ XRF) realizes the measurement of the two-dimensional distribution of elemental compositions (spatial resolution: minimum 25 $\mu$ m) influenced by the cation transfer caused by the corrosion reaction. Namely, when infrared microspectrometry ( $\mu$ FT-IR) and X-ray fluorescence microspectroscopy ( $\mu$ XRF) with a nearly equal spatial resolution are used in a mutually replenishing manner, differently from the conventional electrochemical approach based on electron transfer, corrosion reaction analysis based on element-wise mass transfer is realized.

As described above, based on the surface analysis using soft X-ray synchrotron radiation and two-dimensional mapping analysis using X-ray fluorescence /infrared microspectroscopy introduced in this article, the corrosion reaction and the corrosion-suppressing mechanism of the corrosion products of the Zn-based coated steel sheet formed near the cut-edge surface or a defect part, regarding their compositions, structures and distributions, were clarified. The

clarified corroding and or suppressing mechanisms are expected to contribute to the development of new products and new processes.

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 $[(SST \times 22h + Dry \times 2h) \times 25 times]$ 

Fig. 8 Distribution of O-H bonding in corrosion products near Zn-55% Al/steel interface depended on corrosion environment (5%NaCl aqueous solution and artificial sea water)<sup>19)</sup>

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