Depth Elemental Imaging during Corrosion of Hot-Dip Galvanized Steel Sheet by Confocal Micro XRF Analysis

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Abstract

The elucidation of the mechanism for steel corrosion under a coating layer has been attracting research attention. Herein, we utilized a confocal micro-X-ray fluorescence (XRF) analytical instrument to conduct non-destructive elemental analysis near the surface of a steel sheet. Using this method, elemental map images of steel sheet cross sections were obtained without sample destruction. To confirm corrosion suppression in the presence of Mg ions, we observed the corrosion behavior of hot-dip galvanized steel sheets immersed in aqueous NaCl solution to which Mg ions were added. By using the confocal micro XRF system, the elution of the coating components and the precipitation process of the corrosion products were confirmed.

**Keywords:** Confocal micro XRF, non-destructive elemental analysis, hot-dip galvanized steel sheet, corrosion product.
Introduction

From the perspective of corrosion prevention, the surface of a steel sheet is often coated with a metal and/or a painted film. Surface-treated steel sheets are widely used in automobiles, home appliances, and building materials. However, the anticorrosive effect of a painted film is not permanent. The painted layer gradually deteriorates from the effects of sunlight, wind and rain, and scratches caused by external factors. The effect of a metal coating (typically a zinc-based coating) is also not permanent. Such a coating suppresses steel sheet corrosion via the sacrificial protection effect, but eventually corrosion progresses to the base steel sheet.

Because corrosion reduces the durability of steel sheets, numerous studies have been conducted with the goal of improving corrosion resistance. Understanding the underlying mechanisms of corrosion require detailed observations of the process. These findings would facilitate the development of new surface-treated steel sheets and new materials that are expected to contribute to the continued advancement of technological innovation in related fields.

To observe the corrosion process of surface-treated steel sheets, an accelerated corrosion test is typically performed because of the length of time required to conduct an exposure test in an actual environment. In an accelerated test, the environment is cyclically changed to promote corrosion. A sample’s surface treatment layer, such as a paint film and/or a zinc-based coating, is scratched to the substrate iron and the sample is then exposed to the corrosive environment. The resulting phenomena, such as formation of blisters on a painted layer or elution of a zinc-based coating layer, are not fully understood. Moreover, analysis of the interface between a painted film and a zinc-based coating or between a zinc-based coating and a steel substrate is important.

Because metal corrosion by liquids occurs at the solid-liquid interface, information about
the outer surface of a zinc-based coating contributes to the understanding of corrosion behavior. To analyze surface phenomena, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS), and similar methods have generally been used.\textsuperscript{1-3} However, these methods require cutting the sample to observe its cross section. Non-destructive analysis is usually impossible.

X-ray fluorescence (XRF) spectrometry allows non-destructive, simultaneous multi-element sample analysis.\textsuperscript{4} In conventional XRF, X-ray fluorescence generated within a sample by incident X-rays is observed by EDS. XRF is used to analyze industrial materials, such as semiconductors, plastics, and steel specimens, as well as biological materials, such as soil, hair, blood, art objects, and archaeological samples.\textsuperscript{5, 6} However, XRF spectrometry cannot measurements at a specific depth within a sample are impossible, because the X-ray fluorescence from the sample’s entire depth is detected simultaneously.

Several refinements have improved the utility of XRF. By using a polycapillary lens to focus the incident X-ray beam, a minute area can be analyzed even in a laboratory setting (micro XRF).\textsuperscript{7, 8} Furthermore, two polycapillary lenses have been used to investigate confocal micro X-ray fluorescence analysis has been investigated. The concept of confocal micro X-ray fluorescence analysis was first published by Gibson and Kumakhov in 1993.\textsuperscript{9}

The setup of this analytical method based on two X-ray focusing optics is shown in Figure 1. In this experimental arrangement, a second polycapillary X-ray lens is attached to the detector tip to focus the detection region of the fluorescence signal. The instrument then detects only the X-ray fluorescence generated from the confocal point of the two polycapillary X-ray lenses. Using this method, three-dimensional X-ray fluorescence analysis (3D-XRF) is possible by performing repeated analyses while translating the sample in the xyz directions.\textsuperscript{10, 11}

Previously, we evaluated the characteristics of this procedure experimentally, including the diameter and gain of the micro X-ray beam, by combining an X-ray tube and a polycapillary
X-ray lens. Based on these fundamental studies, a micro XRF system and then a confocal micro XRF system were developed in our laboratory. We have used the latter system to analyze a steel sheet, including in situ observation of corrosion in a solution and observation of light elements under vacuum conditions.

For this report, cross-sectional elemental maps of the corrosion process of hot-dip galvanized steel sheets after saltwater immersion were acquired using a confocal micro XRF system. The instrument visualized changes in elemental distribution as the corrosion process progressed. The visualized elemental maps were significantly different depending on the presence or absence of magnesium ions in the aqueous NaCl solution. Moreover, based on analyses near scratches, the formation of corrosion products containing Mg was confirmed by the presence of magnesium ions.

Experimental

Confocal micro XRF setup

In this study, a confocal micro X-ray fluorescence instrument was used in a vacuum atmosphere. By performing measurements under vacuum conditions, light elements can be efficiently detected. The height, width, and depth of the vacuum chamber were 300 mm × 270 mm × 190 mm, respectively. An air-cooled fine focus X-ray tube (Rh target, MCBM50-0.6B, RTW, Germany) was placed outside the vacuum chamber at an angle of 45 degrees from the sample plane. Using Rh Lα (2.70 keV) contained in primary X-rays emitted from an X-ray tube as an excitation source, we attempted to improve the excitation efficiency of light elements. However, the peaks of Rh Lα (2.696 keV) and Cl Kα (2.622 keV) overlap making detection of the corrosion factor Cl difficult. Therefore, in addition to the normal measurement, an Al filter with a thickness of 30 µm was inserted between the X-ray tube and the polycapillary lens,
removing Rh Lα from the incident X-ray to obtain an elemental map of Cl. The primary X-rays emitted from the X-ray tube were introduced into the vacuum chamber via a Be window. A silicon drift detector (SDD) (Vortex EX-60, Hitachi High-Tech Science Inc., Japan) was used for the detection of X-ray fluorescence. The sensitive area of this detector was 50 mm\(^2\) and the energy resolution was approximately 130 eV for the Mn Kα line (5.90 keV). The total length of the polycapillary X-ray full lens (X-Ray Optical Systems Inc. (XOS), USA) attached to the X-ray tube side was 100 mm, the incident side focal length was 30 mm, and the exit side focal length was 2.5 mm. For the detector side, a polycapillary X-ray half lens (X-Ray Optical Systems Inc. (XOS), USA) was attached to the top of the SDD. The total length of this lens was 36 mm and the focal length was 3.0 mm. The SDD and the polycapillary X-ray full lens were each arranged at the angle of 45 degrees from the sample plane.

A sample was set horizontally on an xyz translation stage (XA04A-R2-1J and ZA07A-R3S-2H, Kohzu Precision Co., Ltd., Japan). The sample stage operated with a displacement of ± 5 mm in the xy direction and ± 12 mm in the z direction. A color CCD camera (20× magnifications, focal length 140 mm, TOSHIBA Teli Co., Japan) was attached to the viewing window at the top of the vacuum chamber and used to adjust the measurement position.

The spatial resolution of the confocal micro-XRF system depends on the size of the confocal point.\(^{16}\) A resolution of approximately 12 µm was obtained at 18 keV. However, at lower energies, the resolution deteriorates. Such energy dependence is caused by the total reflection of X-rays at the polycapillary lens. As the incident X-ray energy decrease, the critical angle for total reflection increases and the beam size at the focal point expands. As a result, the size of the confocal point increases and the resolution deteriorates. The measurement results for light elements, such as Cl and Mg, should be interpreted with caution.
Sample preparation

Hot-dip galvanized steel sheets were used as test specimens. The weight of the zinc coating was 135 g/m². The back and end faces of each test specimen were masked with polyester insulating tape. To observe the corrosion behavior when the zinc coating layer was damaged, the center of the test specimen was scratched to expose the iron substrate. A confocal micro XRF system was used to obtain a cross-sectional view of a portion of the specimen including the scratch. The test specimen was then immersed in an aqueous NaCl solution. An image of the sample and a schematic diagram of the specimen cross section are shown in Figure 2. To analyze the same position of each sample consistently, the stage shown in Figure 2 (c) was used to fix the sample alignment. Two of the four sides of the test specimen were placed in close contact with the stage so that the test specimen was placed in the same alignment each time.

In this study, two kinds of aqueous solutions were prepared for immersion of the test specimens: a 5% NaCl aqueous solution and a NaCl aqueous solution with added Mg ions at roughly the concentration (approximately 0.3%) of Mg ions in seawater. The temperature of the test aqueous solutions was set to 55 °C. After immersion for 24 h, the test specimen was removed, washed with deionized water, dried, and then XRF measurements were performed. After the measurements, the test specimen was again immersed and the procedure was repeated to visualize changes in the elemental distribution as corrosion progressed.

Confocal micro XRF measurement

XRF measurements were performed every 24 h for 120 h. The XRF measurement area was 700 µm in the direction across the scratch (x axis) and 300 µm in the depth direction (z axis). The step size was 10 µm for both the x and z axes. The acquisition time was 20 seconds per point, and the total measurement time for one field of view was about 12 h. All measurements were performed under vacuum conditions of around 1 Pa. The measured
elements included Zn, which is a constituent element of the coating; Fe from the base steel sheet; and Cl derived from the NaCl aqueous solution. In addition, Mg was also measured under the same conditions under which Mg ions were added. By comparing the results for these two aqueous solution conditions, we were able to confirm that Mg ions suppressed corrosion when added to the aqueous NaCl solution.

Analysis of corrosion product

The corrosion products that had formed on a test specimen scratch after 120 h immersion were scraped off and identified by powder X-ray diffraction (XRD). The XRD measurements were performed using a Co target (Rint 2500H/PC, Rigaku Co., Ltd., Japan). The tube voltage was set to 30 kV. The measurement angle range was from 5 degrees to 105 degrees in 2θ, and the angle step was 0.02 degrees.

Results and Discussion

Figure 3 represents elemental maps of the test specimen cross sections, where the x axis indicates the direction across a scratch and the z axis indicates the depth direction. Along the z axis, 300 µm indicates the surface of the test specimen and 0 µm indicates the inner side of the test specimen. Figures 3 (e), (f), (g), and (h) are the elemental maps of Zn before immersion and 24 h, 72 h, and 120 h after immersion, respectively. From the elemental map of Zn before immersion (e), it can be confirmed that Zn in the hot-dip galvanized layer was completely removed by the scratch, which suggests that the iron substrate was exposed. After immersion for 24 h (f), the elemental map confirmed that Zn was eluted from a region of the zinc coating layer. The elution of Zn was clearly observed after 72 h (g) and 120 h (h), and the elemental distribution of Zn changed significantly throughout the immersion process over a period of 120
Figures 3 (a)–(d) show the elemental maps of Fe before immersion and 24 h, 72 h, and 120 h after immersion, respectively. Fe was detected at approximately 150 µm along the z axis. This element is also present at depths in excess of 150 µm, but its signal was not detected at greater depths owing to self-absorption. Based on the elemental map before immersion (a), the steel substrate was deformed due to the scratch. From the elemental maps at 24 h (b), 72 h (c), and 120 h (d), it was determined that the distribution of Fe did not change significantly during immersion for 120 h. This is likely due to the sacrificial corrosion effect, whereby Zn in the hot-dip galvanized layer is preferentially eluted to protect Fe.

Figures 3 (i)–(k) show the elemental maps of Cl 24 h, 72 h, and 120 h after immersion, respectively. The elemental maps of Zn and Cl showed correspondences between their distributions. After 72 h (j) and 120 h (k), the Cl intensity exhibited higher correspondence with the areas in which eluted Zn had accumulated. This suggests that eluted Zn and Cl produce corrosion products. The mechanism of zinc corrosion in a seawater environment is considered to proceed according to the following equation.\(^{21,22}\)

\[
\begin{align*}
\text{Anode) } & \quad \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \\
\text{Cathode) } & \quad \text{1/2O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \\
\text{Corrosion products) } & \quad 5\text{Zn}^{2+} + 2\text{Cl}^- + 8\text{OH}^- \rightarrow \text{ZnCl}_2\cdot 4\text{Zn(OH)}_2 \\
\text{Overall) } & \quad 5\text{Zn} + 5\text{H}_2\text{O} + 5/2\text{O}_2 + 2\text{Cl}^- \rightarrow \text{ZnCl}_2\cdot 4\text{Zn(OH)}_2 + 2\text{OH}^- 
\end{align*}
\]

Elemental maps of Fe, Zn, Cl, and Mg for specimens immersed in the presence of Mg ions are shown in Figure 4. The x axis indicates the direction across a scratch, and the z axis indicates the depth direction. Figures 4 (e)–(h) show the elemental maps of Zn before immersion and 24 h, 72 h, and 120 h after immersion, respectively. The Zn distribution is in clear contrast to its distribution when Mg ions are not present. Before immersion (e), the hot-dip
galvanized layer was completely removed from the Fe substrate. However, from 24 h after immersion (f), the map shows that Zn was present to cover the scratch. This phenomenon is also observed after 72 h (g) and 120 h (h) and probably protects the exposed areas of the steel substrate.

Figures 4 (a)–(d) show the elemental maps of Fe before immersion and 24 h, 72 h, and 120 h after immersion, respectively. As when Mg ions are not present, no significant change was observed for the Fe distribution after 120 h immersion.

Figures 4 (i)–(k) show the elemental maps of Mg 24 h, 72 h, and 120 h after immersion, respectively. In the elemental map after 24 h immersion (i), as was the case with Zn, Mg was distributed so that the scratch was covered. At 72 h (j) and 120 h (k) after immersion, the intensity of Mg Kα on the scratch increased, indicating that more Mg was present.

Figures 4 (l)–(n) show the elemental maps of Cl 24 h, 72 h, and 120 h after immersion, respectively. The maps confirm that Cl, which is a corrosion factor, was also distributed at positions corresponding to Zn and Mg. These results suggest that Mg also exists as a corrosion product. The presence of added Mg ions appears to suppress the corrosion of the iron substrate compared to conditions without Mg ions, because the corrosion products, which consist of Zn, Cl, and Mg completely cover the scratch and the iron substrate. To confirm this assertion, we continued the immersions and noted timing, for each sample, of the occurrence of red rust, indicating iron substrate corrosion.

The powder XRD measurement results of the corrosion product from the scratched area after 120 h immersion are shown in Figure 5. Figure 5 (a) shows the results for 5% NaCl and Figure 5 (b) the results with added Mg ions. Under 5% NaCl conditions (a), triplet peaks of zinc oxide (ZnO) and peaks of basic zinc chloride (Zn₅(OH)₆Cl₂·H₂O) and basic zinc carbonate (Zn₅(CO₃)₂(OH)₆) were observed. The peak of metallic zinc was also confirmed. We determined that basic zinc chloride had formed, as shown in the above reaction sequence (1)–(4).
However, under conditions of added Mg ions (b), in addition to zinc oxide and metal Zn, peaks of Mg hydroxide were also detected. We concluded that the following reaction had occurred, resulting in corrosion products.

\[
\text{Corrosion products: } \text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \quad (5)
\]

In addition, a peak attributed to magnesium chloride hydroxide hydrate (\(\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}\)) was confirmed at a lower angle. Moreover, the peak corresponding to basic zinc chloride exhibited a slight shift, suggesting that a partial substitution with Mg had occurred with a corresponding change in the lattice constant.

**Conclusions**

A confocal 3D-XRF system combining two polycapillary lenses in a vacuum was used to non-destructively observe the corrosion of the hot-dip galvanized steel sheet in NaCl solution. Elemental maps of test specimens were obtained using this instrument. The spatial resolution of the confocal 3D-XRF system was sufficient to distinguish between the coating layer and the steel substrate. By performing measurements under vacuum conditions, elemental maps of light elements, such as Mg and Cl, were acquired. The preferential elution of Zn in the coating layer, owing to the sacrificial anticorrosion effect of Zn, was visualized based on the Fe and Zn elemental maps of the cross section. Use of this instrument allowed us to observe clearly that with added Mg ions in the solution, Cl and Mg together with Zn produced corrosion products near a scratch. The element identifications were confirmed that it corresponded to the constituent elements of the corrosion products identified by XRD analysis. The results obtained in this study highlight the advantage of confocal micro-XRF analysis: it can be used without sample destruction to obtain cross-sectional elemental maps, which can be used in the analysis...
of corrosion processes under a coating layer. This analysis method is an effective means of elucidating the corrosion mechanism at the solid-liquid interface between a Zn coating layer and its base steel substrate.

Acknowledgements

A part of this work was supported by JSPS KAKENHI Grant Number 17H03080

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Figure Captions

Fig. 1  Principle of confocal three dimensional X-ray fluorescence (3D-XRF) analysis.

Fig. 2  (a) Image of a test specimen. (b) Schematic image of the cross section of a test specimen. (c) Image of the position fixing stage.

Fig. 3  Non-destructive cross-sectional elemental mapping of Zn, Fe, and Cl after immersion in 5% NaCl aqueous solution. The measurement range was 700 µm (across the scratch) × 300 µm (depth). Images (a), (b), (c), and (d) show the elemental maps of Fe before immersion and after 24 h, 72 h, and 120 h, respectively. Images (e), (f), (g), and (h) show the elemental maps of Zn before immersion and after 24 h, 72 h, and 120 h, respectively. Images (i), (j), and (k) show the elemental maps of Cl after 24 h, 72 h, and 120 h, respectively.

Fig. 4  Non-destructive cross-sectional elemental mapping of Zn, Fe, Cl, and Mg after immersion in 5% NaCl aqueous solution with added Mg ions. The measurement range was 700 µm (across the scratch) × 300 µm (depth). Images (a), (b), (c), and (d) show the elemental maps of Fe before immersion and after 24 h, 72 h, and 120 h, respectively. Images (e), (f), (g), and (h) show the elemental maps of Zn before immersion and after 24 h, 72 h, and 120 h, respectively. Images (i), (j) and (k), show the elemental maps of Cl after 24 h, 72 h, and 120 h, respectively. Images (l), (m), and (n) show the elemental maps of Mg after 24 h, 72 h, and 120 h, respectively.

Fig. 5  Powder X-ray diffraction (XRD) measurement results for the corrosion products collected near the scratch. The upper pattern shows the result obtained with the NaCl solution. The lower pattern shows the results with Mg ions added to the NaCl solution.
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Fig. 5 Powder X-ray diffraction (XRD) measurement results for the corrosion products collected near the scratch. The upper pattern shows the result obtained with the NaCl solution. The lower pattern shows the results with Mg ions added to the NaCl solution.