

FUNDAMENTAL STUDY ON CORROSION PROPERTIES OF HOT-DIP ALUMINUM COATING ON STEEL STRUCTURES

高, 揚

<https://hdl.handle.net/2324/7329488>

出版情報 : Kyushu University, 2024, 博士 (工学) , 課程博士
バージョン :
権利関係 :



**FOUNDAMENTAL STUDY ON CORROSION
PROPERTIES OF HOT-DIP ALUMINUM COATING
ON STEEL STRUCTURES**

Yang Gao

FUNDAMENTAL STUDY ON CORROSION PROPERTIES OF HOT-DIP ALUMINUM COATING ON STEEL STRUCTURES

A Thesis Submitted
In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Engineering

By
Yang Gao



九州大学

to the
DEPARTMENT OF URBAN AND ENVIRONMENTAL ENGINEERING
GRADUATE SCHOOL OF ENGINEERING
KYUSHU UNIVERSITY

Fukuoka, Japan
September, 2024

DEPARTMENT OF URBAN AND ENVIRONMENTAL ENGINEERING
GRADUATE SCHOOL OF ENGINEERING
KYUSHU UNIVERSITY
Fukuoka, Japan

CERTIFICATE

The undersigned hereby certify that they have read and recommended to the Graduate School of Engineering for the acceptance of this Thesis entitled, “*Fundamental Study on Corrosion Properties of Ho-dip Aluminum Coating on Steel Structures*” by **Yang Gao** in partial fulfillment of the requirements for the degree of **Doctor of Engineering**.

Dated: March, 2024

Thesis Supervisor:

Prof. Shigenobu Kainuma, Dr. Eng.

Examining Committee:

Prof. Hiroaki Nakano, Dr. Eng.

Prof. Chihiro Morita, Dr. Eng.

ABSTRACT

Hot-dip aluminum coating is a simple and efficient surface coating technique. Steel, when treated with hot-dip aluminum, gains enhanced corrosion resistance, weather resistance, and anti-oxidation properties, thus reducing significant economic losses caused by steel corrosion. It also prolongs the lifespan of steel materials, leading to improved economic benefits. Atmospheric corrosion is the most common form of corrosion failure in steel structures. This study evaluates the anti-corrosion performance of hot-dip aluminum in atmospheric environments through practical atmospheric corrosion experiments.

The outermost layer of pure aluminum in hot-dip aluminum coatings is susceptible to passivation. In general, it functions as a cathodic coating except in environments with high chloride ion concentrations. When there are defects in the coating, it fails to provide effective protection to the substrate. To enhance the sacrificial anode performance, a 55Al-Zn coating has been developed, but its corrosion resistance is notably lower than that of hot-dip aluminum.

In this study, some kinds of atmospheric types were researched by the atmospheric exposure test. The corrosion behavior of hot-dip aluminum was evaluated by the actual atmospheric environment. The atmospheric types include coastal environment, urban atmospheric environment, and alkaline environment. An eight-year atmospheric exposure experiment was conducted to compare the performance of aluminum-based coatings with traditional zinc coatings. Hot-dip aluminum exhibited significant advantages in typical atmospheric exposure conditions. Hot-dip aluminum structures exhibit excellent corrosion resistance in atmospheric environments. However, in environments with high salt concentrations, aluminum layers tend to degrade in high chloride ion environments.

Similarly, in steel structure construction where hot-dip aluminum is applied, bolts are often used for connections. The hot-dip aluminum process involves relatively high bath temperatures, which can lead to a reduction in axial force in the bolts. As a result, other coatings with thinner layers and less thermal impact, such as 55Al-Zn and Zn, are often used for bolt dipping. When different metals come into contact in a solution environment, they can undergo galvanic corrosion. Electrochemical experiments and atmospheric

exposure tests were conducted to investigate the galvanic corrosion between hot-dip aluminum, 55Al-Zn, Zn, and stainless bolts. The experiments indicated that the sacrificial anode reaction was least apparent in the case of 55Al-Zn, suggesting that it is a better choice for use in conjunction with hot-dip aluminum.

Subsidiary structures in bridge construction typically use hot-dip aluminum, which may come into contact with concrete materials. The feasibility of hot-dip aluminum coming into contact with concrete was studied through a two-year atmospheric exposure experiment. The exposure test indicated that the hot-dip aluminum coating steel structure can't be used in fresh concrete but can be used in hardened concrete for a long time.

TABLES OF CONTENTS

ABSTRACT	i
TABLES OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER 1 INTRODUCTION	1
1.1 Background	1
1.2 Objectives and scope	3
1.3 Literature review	5
1.3.1 Development of hot-dip aluminum technology	5
1.3.2 The structure and formation mechanism of hot-dip aluminum coating	5
1.3.3 Performance and applications of hot-dip aluminum coatings	6
1.4 Organization and outline	8
CHAPTER 2 LONG-TERM CORROSION PROPERTIES OF HOT-DIP ALUMINUM COATING EXPOSURE IN COASTAL ATMOSPHERIC ENVIRONMENT	11
2.1 Introduction	11
2.2 Experimental	12
2.2.1 Monitoring steel plate (MSP) assessment	12
2.2.2 Cross-sectional analysis of core specimens	16
2.2.3 Electrochemical measurement	16
2.3 Results	16
2.3.1 The environment assessment by MSPs	16
2.3.2 Backscattered electron image (BSE) and EPMA analysis	18
2.3.3 Electrochemical properties of hot-dip aluminum coating	21
2.4 Deterioration mechanism of hot-dip Al coating	22
2.5 Summary	28

CHAPTER 3 ATMOSPHERIC EXPOSURE TEST OF HOT-DIP	
ALUMINUM COATING.....	29
3.1 Introduction.....	29
3.2 Experimental	30
3.3 The surface condition of the specimens after the atmospheric exposure test.	34
3.4 Evaluation of corrosion behavior after long-term atmospheric exposure test.	41
3.4.1 SEM-EDX surface elements analysis	41
3.4.2 SEM-EDX corrosion section elements analysis	42
3.5 Consideration of hot-dip Al coating in the atmospheric environment.	46
3.5.1 Overview of the corrosion of Al in the atmospheric environment...	46
3.5.2 The effect of the environmental factors.....	48
3.5.3 Corrosion characteristics of pitting corrosion.....	50
3.6 Summary	52
CHAPTER 4 GALVANIC CORROSION BEHAVIOR OF HOT-DIP	
ALUMINUM AND METAL COATINGS APPLIED TO	
STEEL BOLTED JOINTS	53
4.1 Introduction.....	53
4.2 Experimental	56
4.2.1 Specimens.....	56
4.2.2 Electrochemical test	56
4.2.3 Atmospheric exposure test.....	58
4.2.4 Surface condition and cross-sectional analyses.....	59
4.3 Electrochemical test results of hot-dip aluminum coating.....	60
4.3.1 Potential-time and galvanic current measurements of specimens ...	60
4.3.2 Galvanic corrosion current in the theory calculation	62
4.4 Corrosion behavior of hot-di aluminum coating in the atmospheric exposure	
test.....	70
4.5 Summary	74
CHAPTER 5 CORROSION BEHAVIOR OF HOT-DIP ALUMINUM	
COATING CONTACT WITH CONCRETE	75
5.1 Introduction.....	75

5.2	Corrosion behavior of hot-dip aluminum contact with fresh concrete.....	76
5.3	The pH changes of concrete during the hardening process	79
5.4	Analysis of hot-dip aluminum coating after atmospheric exposure test	81
5.5	The corrosion behavior of Al coating contact with concrete	88
5.6	Summary	93
CHAPTER 6 CONCLUSIONS AND FUTURE WORK		94
6.1	Main conclusions and innovations	94
6.2	Summary	94
6.2.1	The galvanic corrosion of hot-dip Al coating applied to bolted joints	95
6.2.2	The corrosion behavior of hot-dip Al coated steel plate contact with concrete	95
6.2.3	Long-term corrosion behavior of hot-dip Al coating exposure in the atmospheric environment.....	95
6.2.4	The mechanical properties of hot-dip Al coated steel plate.....	96
6.3	Recommendations for the future work	96
REFERENCES.....		98
ACKNOWLEDGEMENT		116
APPENDIX		
CHAPTER 7 MECHANICAL PROPERTIES OF HOT-DIP COATED STEEL PLATE.....		118
7.1	Introduction.....	118
7.2	Experimental	119
7.3	Tensile test results.....	121
7.4	Fractography and fracture mechanism of specimens	126
7.5	Summary	133

LIST OF TABLES

Table 2-1 Chemical compositions of MSP (wt.%)	12
Table 2-2 Attached positions of MSPs in trestle.....	13
Table 2-3 Corrosion potential E_{corr} (V vs.Ag/AgCl) and corrosion current density i_{corr} (A/cm ²).....	22
Table 3-1: The atmospheric data of the exposure sites.	32
Table 4-1 Specimens exposed in the University of the Ryukyus (UR) and Kyoda (KY).	56
Table 4-2 Environmental data of the two exposure sites measured by EL-USB-2 sensor (Lascar Electronics Inc.) (2017–2021)	59
Table 4-3 Elemental distributions in UR and KY specimens on the cross-section perpendicular to the front surface.....	72
Table 5-1. Concrete compositions (kg/m ³).....	77
Table 5-2. Atmospheric environment of Kyoda (KY), University of the Ryukyus (UR), and Kyushu University (KU) sites.	81
Table 5-3. SEM image and EDS analysis of cross section after exposure test.	87
Table 7-1. Types of specimens in tensile test.	119

LIST OF FIGURES

Fig. 1-1 The hot-dip coating process.	3
Fig. 1-2 The flowchart of the dissertation.	10
Fig. 2-1 Inspection device for maintain management of bridge substructure.	55
Fig. 2-2 Configuration of the galvanic current test.	57
Fig. 2-3 Location of the exposure sites.	58
Fig. 2-4 Surface appearance of exposed specimens.	58
Fig. 2-5 Sample of exposure test after cutting and polishing.	59
Fig. 2-6. Change in total galvanic currents for the Al and 55Al–Zn circuits with time at different area ratios.	60
Fig. 2-7 Measurement of the OCP for Al and 55AlZn in the 0.1 wt% and 3.5 wt% NaCl solutions.	61
Fig. 2-8 Galvanic current density of Al and 55Al–Zn circuits in 0.1 wt% and 3.5 wt% NaCl solutions.	62
Fig. 2-9 Metal resistance measurement system.	63
Fig. 2-10 Conductivity of NaCl solution in different concentrations.	65
Fig. 2-11 Change in solution resistance and galvanic current density with the change in NaCl concentration.	65
Fig. 2-12 Galvanic current density in 0.1 wt% and 3.5 wt% NaCl solutions.	66
Fig. 2-13 Observation of the surface before and after the electrochemical test.	67
Fig. 2-14 Schematic of the galvanic corrosion during the electrochemical test.	68
Fig. 2-15 Change in mass loss with different area ratios.	70
Fig. 2-16 Schematic and cross-section of the exposure test.	70
Fig. 2-17 Element distribution obtained by SEM-EDS on the cross-section of the outside and interlining parts.	73
Fig. 3-1 The dimensions and cross-sectional view of MSP specimen.	13
Fig. 3-2 The location and overview of the trestle in Kagoshima oil terminal.	15
Fig. 3-3 Schematic diagram of the attachment method of MSP specimens.	15
Fig. 3-4 The attachment locations of MSP specimens (unit: mm)	15
Fig. 3-5 The mean corrosion depth of MSP specimens.	17

Fig. 3-6 The rust thickness of MSP specimens.....	18
Fig. 3-7. BSE images of core specimens and the element distribution obtained by EPMA on the cross-section.	20
Fig. 3-8 OCP of aluminum layer and Fe-Al intermetallic layer	21
Fig. 3-10 Schematics showing the thickness of aluminum layer, Fe-Al intermetallic layer, steel substance.....	23
Fig. 3-11 Cross-sectional micrograph and EDS analysis of core specimen get from Kagoshima trestle	24
Fig. 3-12. Cross-sectional micrograph and EDS analysis of core specimen get from Kagoshima trestle.	24
Fig. 3-13. Open circuit potential of aluminum, Al-Fe intermetallic, Fe specimens in four concentrations of NaCl solution	26
Fig. 3-14 The BSE image and schematic diagram of corrosion process.....	27
Fig. 4-1 The contact of hot-dip Al coated steel member and concrete in the actual situation.....	76
Fig. 4-2 Interface cross section observation of round bar and mortar.	78
Fig. 4-3 The variation of OCP with the change of pH for the Al coating.	79
Fig. 4-4 The pH changes with the curing age.....	80
Fig. 4-5. The scene and schematic diagram of specimens in the exposure site.....	81
Fig. 4-6 Appearance of the exposed specimens after 2.5 years of exposure.	83
Fig. 4-7 The corrosion products analysis by XRD analysis.	84
Fig. 4-8 The surface element concentration evaluation of the specimens after the exposure test.	86
Fig. 4-9 The corrosion behavior of Al-coated steel plate contact with concrete.	88
Fig. 5-1 The size of the specimen in the atmospheric test.	31
Fig. 5-2 The Cross-sectional of the defect part on specimens for atmospheric exposure test.....	31
Fig. 5-3 The location of exposure sites.	32
Fig. 5-4 Photographs of the atmospheric exposure test sites.	33
Fig. 5-5 The surface condition of Al and 55Al-Zn coatings in exposure test.	37
Fig. 5-6 Schematic diagram of hot-dip aluminum production process.....	38

Fig. 5-7 The surface condition of hot-dip Zn coating after atmospheric exposure test. .	40
Fig. 5-8 Surface mapping of hot-dip Al coating specimen after atmospheric exposure test in KY and UR.....	41
Fig. 5-9 Cross-section mapping of hot-dip Al coating specimen after atmospheric exposure test in KY and UR.....	44
Fig. 5-10 Common forms of pitting corrosion development.....	50
Fig. 7-1. Schematic diagram of the specimens in the tensile test.	120
Fig. 7-2 Photograph of specimen in tensile test.....	120
Fig. 7-3 The cracking and debonding of coatings after tensile test.	122
Fig. 7-4 Load and displacement curves.....	122
Fig. 7-5 Load and displacement curves of three kinds of hot-dip coatings.	123
Fig. 7-6 The mechanical properties of hot-dip coatings in tensile test.	124
Fig. 7-7 The hardness test of hot-dip Al coating tensile test.	125
Fig. 7-8 The fracture surface microstructure of the hot-dip Al coating specimen.....	126
Fig. 7-9 The SEM-EDS analysis of the brittle fracture.....	127
Fig. 7-10 The line analysis of the element in the brittle fracture zone.	127
Fig. 7-11 Schematic side view representation of multiple cracking of coatings.	129
Fig. 7-12 Optical micrographs of cross section hot-dip Al coating on the steel substrate.	129
Fig. 7-13 The crack and debonding process of hot-dip Al coating in tensile test.....	130

CHAPTER 1 INTRODUCTION

1.1 Background

Steel is widely used in various fields such as machinery, construction, and appliances due to its large production, relatively low cost, and excellent mechanical properties [1–4]. However, steel is highly susceptible to corrosion in nearly all environments. Corrosion rates are even faster in corrosive and high-temperature oxidative environments [5]. For this reason, a significant amount of steel materials, machinery, and steel components are discarded each year due to corrosion. During the use of steel, two main types of corrosion occur: chemical corrosion (involving chemical substances such as SO_2 , Cl_2 , O_2 , which undergo oxidation-reduction reactions) and electrochemical corrosion (reacting with electrolyte solutions, causing the metal to lose electrons and undergo oxidation reactions) [6–8]. Chemical corrosion primarily includes hydrogen embrittlement and oxygen absorption corrosion. Corrosion prevention techniques refer to various methods employed to extend the lifespan of metal products exposed to corrosive media, ensuring the safety and smooth operation of process equipment. Corrosion prevention measures involve altering the metal itself, surface treatment, and environmental modifications [9,10]. Common corrosion prevention methods include: Structural modification: Incorporating chromium, nickel, and other elements into ordinary steel to create stainless steel, thereby enhancing its corrosion resistance. However, this approach is costlier and less suitable for large-scale applications. Coating method: Applying protective coatings on the metal's surface to isolate it from the corrosive medium, thus preventing corrosion [11–13]. Electrochemical protection method: Using the principles of galvanic cells to protect the metal by eliminating the galvanic cell reactions that lead to electrochemical corrosion. This method includes sacrificial anode protection and cathodic protection [14–16]. Altering the corrosion environment: Modifying the environmental conditions in which the steel is situated, such as temperature, humidity, and pH levels. Methods for creating protective layers on metals include electroplating, hot-dip coating, thermal spraying, and chemical plating. Among these, hot-dip coating stands out due to its low cost, high production yield, excellent coating stability, and extended coating service life. Hot-dip

zinc and its alloys are the most common and economically efficient corrosion prevention techniques for steel materials in atmospheric environments [17,18].

Hot-dip galvanizing provides the following corrosion protection effects for steel materials: Isolation protection: The coating effectively isolates the steel from corrosive media, preventing direct erosion of the steel. Cathodic protection: The coating serves as an ideal protective layer for steel surfaces [19,20]. Apart from its lower corrosion rate compared to steel in atmospheric and aqueous environments, it also has a more negative corrosion potential than iron. This allows it to provide cathodic protection to the steel, ensuring that the coated parts remain protected from corrosion, even in areas where galvanization is absent or where the coating has been damaged. Corrosion product protection: During the corrosion process of the coating, various corrosion products are formed on the surface of the coating. These products not only consume the corrosive medium but also prevent further penetration, effectively isolating the corrosive medium from the coating. This has a protective effect on both the coating and the steel, contributing to the longer service life of hot-dip galvanized steel components [21,22]. Hot-dip galvanizing is the most widely used material in hot-dip coatings. However, due to zinc's susceptibility to dissolution and its low melting point, it cannot be used for extended periods in certain harsh or high-temperature environments [7,23]. With the continuous expansion of the application areas of hot-dip galvanized products, its performance gradually fails to meet the corrosion protection requirements. As a result, hot-dip aluminum coating was later developed to replace hot-dip galvanizing [18].

Among the various hot-dip coating materials, hot-dip galvanizing of steel effectively slows down steel corrosion, extends its service life, and offers a production process that is cost-effective, simple, and results in reliable and aesthetically pleasing coatings. As a result, hot-dip galvanized steel is widely used. However, traditional galvanized coatings have relatively lower corrosion resistance, especially in marine environments, industrial settings, and high-temperature conditions. The addition of other elements such as Al, Mg, Si, RE, and others to the alloy can enhance the coating's corrosion resistance and formability while reducing the coating thickness [23–25]. As a result, the composition of coatings has gradually shifted from pure zinc towards zinc alloys and pure aluminum.



Fig. 1-1 The hot-dip coating used in the trestle bridge.

1.2 Objectives and scope

Research on hot-dip aluminum coating technology has achieved certain results, but it's evident from the current state of research that there are still issues with this technology. Concerning its corrosion resistance, the protective mechanism of hot-dip aluminum layers on the substrate should involve sacrificial anodic protection. While hot-dip aluminum has its advantages compared to hot-dip galvanizing, pure aluminum on the surface of hot-dip aluminum coatings is prone to passivation. Except in environments with higher Cl⁻ content, it generally functions as a cathodic coating and cannot provide effective cathodic protection to the substrate in the presence of coating defects [26,27]. Subsequently, an alloy coating, 55Al-43.4Zn-1.6Si, was developed with sacrificial anode properties across all media [24,25]. However, the corrosion resistance of the 55Al-Zn alloy coating is noticeably lower than that of pure hot-dip aluminum. This study conducts a comprehensive investigation into the corrosion resistance performance of hot-dip aluminum and compares it horizontally with 55Al-Zn and Zn coatings.

This dissertation is organized based on the objectives listed below:

- (1) A study was conducted on the performance of hot-dip aluminum-coated steel structures in a nearshore marine environment, utilizing a practical gantry beam with a 25-year-old hot-dip aluminum coating. Various sampling points were selected, and samples were collected, followed by corrosion assessment using microscopic observation. The corrosion process and mechanisms were summarized based on observations of both mild and severe corrosion conditions.

-
- (2) The corrosion behavior of hot-dip aluminum in different types of atmospheric environment was studied by the atmospheric exposure test. A eight years long - term atmospheric exposure test was carried out in 5 exposure sites. The environment types contain high airborne salt environments, rainy washing environments, and without rainy washing environments. Also can be described as far sea and near sea environment. The objective corrosion behavior can be formulated by the exposure test.
- (3) The connection between hot-dip aluminum-coated components and 55Al-Zn/Zn bolts can experience galvanic corrosion due to the dissimilar metals involved, as different metals possess varying electrical potentials. An electrochemical approach was employed to study the mechanism of galvanic corrosion. Research was conducted on the galvanic corrosion behavior in real-world environments by fastening hot-dip aluminum steel plates to 55Al-Zn, Zn, and stainless steel bolts. A four-year atmospheric exposure experiment confirmed the presence of galvanic corrosion and evaluated the corrosion behavior of bolts made of different materials in various atmospheric conditions.
- (4) In the case of hot-dip aluminum used in the auxiliary structures of bridges, it comes into contact with concrete. However, aluminum is an amphoteric oxide, which means it can react with both acidic and alkaline substances. Concrete is a typical alkaline material. Whether corrosion occurs between the two during their use was verified through a two-year atmospheric exposure experiment. This study also provided a basis for determining whether hot-dip aluminum can be used in contact with concrete.
- (5) The high-temperature environment in the production process of hot-dip aluminum can have a certain impact on the mechanical properties of steel structures. The influence of hot-dip aluminum on the mechanical properties of steel was assessed through tensile testing. The reasons for the changes in mechanical properties were evaluated through microscopic analysis was shown in the appendix.

1.3 Literature review

1.3.1 Development of hot-dip aluminum technology

Before 1890, people gradually recognized that coating steel materials with aluminum created new materials with the strength of steel and the characteristics of aluminum [28,29]. After 1893, German scientists published the first papers on hot-dip aluminum, formally introducing the concept of hot-dip aluminum [30]. Subsequently, German scientist A. Hüttmann's research report on the heat resistance of hot-dip aluminum-coated steel was published, leading to the gradual expansion of the production and application of hot-dip aluminum steel materials [31]. In 1939, the American Armco Steel Corporation converted an existing continuous hot-dip galvanizing production line for use in producing hot-dip aluminum-coated steel strips [32,33]. From that point, hot-dip aluminum technology entered the era of large-scale industrial applications.

In 1949, G.A. Moller patented the solvent-based hot-dip aluminum process, and in 1955, the American Chain Cable Company invented the water-based hot-dip aluminum technology, further advancing hot-dip aluminum technology [34,35]. After 1970, the demand for hot-dip aluminum-coated steel materials sharply increased due to their excellent corrosion resistance in harsh environments like high temperatures and seawater [36].

1.3.2 The structure and formation mechanism of hot-dip aluminum coating

After the aluminum coating process, the resulting coating consists of two layers: an outer layer of pure aluminum and an inner layer of an alloy. The composition of the aluminum layer is nearly identical to that of liquid aluminum, while the alloy layer's composition depends on the composition of the liquid aluminum. The inner Fe-Al alloy layer is FeAl_3 and Fe_2Al_5 when the dipping time is relatively short [37–39]. However, when the dipping time is longer, only Fe_2Al_5 is present, and other intermetallic compounds such as FeAl_2 and FeAl_3 are not observed. Fe_2Al_5 is the primary phase in the Fe-Al alloy, and its morphology shows a tongue-like structure that penetrates into the substrate vertically, perpendicular to the surface of the coated object [37,40]. There is a well-defined interface between Fe_2Al_5 and the substrate, without any transitional regions containing other compounds or solid solutions. This suggests that the growth of the alloy layer during the hot-dip aluminum process is quite unique.

1.3.3 Performance and applications of hot-dip aluminum coatings

Mechanical Properties: Hot-dip aluminum coating on steel has no significant impact on the overall mechanical properties of the material [41,42]. Yield strength, tensile strength, and elongation remain relatively unchanged, but creep strength shows a noticeable improvement. The toughness of the aluminum coating decreases, and the hardness of the alloy layer reaches HV600-750. Through proper processing techniques, the mechanical properties of hot-dip aluminum-coated steel can meet the required standards.

Corrosion Resistance: Hot-dip aluminum coatings provide excellent protection for steel substrates. The aluminum coating not only acts as a sacrificial anode for electrochemical protection of the steel but also forms a dense and stable aluminum oxide (Al_2O_3) surface layer. This oxide layer maintains passivation, preventing continuous oxidation in atmospheric conditions and isolating the corrosive media [23,43–45]. This significantly extends the service life of steel structures. Hot-dip aluminum coatings also demonstrate good corrosion resistance in highly polluted environments containing sulfides, carbon dioxide, ammonia, sulfur dioxide, moisture, and dust. They perform exceptionally well in resisting sulfur-containing gas corrosion, making them the preferred choice for this application.

Oxidation Resistance: The oxidation resistance of hot-dip aluminum coatings depends on the coating thickness and the aluminum content on the surface [46,47]. Generally, hot-dip aluminum-coated steel can withstand temperatures 200-300°C higher than uncoated steel, allowing it to be used at 800°C for long-term exposure and briefly at 1000°C [46,48]. Numerous oxidation tests have demonstrated a significant improvement in the high-temperature oxidation resistance of hot-dip aluminum-coated steel. Additionally, hot-dip aluminum-coated steel exhibits good solar reflectance, maintaining its reflective capability even after exposure to atmospheric conditions [23,49].

Aluminizing Process Improvements: By employing co-diffusion treatments, it is possible to increase the thickness of the alloy layer on the coated object's surface. This improves the toughness, plastic deformation ability, and reduces the hardness of the alloy layer while minimizing defects within the alloy layer, ultimately enhancing its wear resistance [20,50,51].

Formability: Hot-dip aluminum-coated plates can undergo moderate deformation without coating cracking or delamination. Reducing the thickness of the intermediate alloy layer can further improve the formability of the coating [24,52,53].

Applications: Hot-dip aluminum coatings, in addition to their excellent performance, are known for their simplicity in processing. They do not require vacuum or low-temperature conditions, have minimal pre-processing requirements, offer high processing capacity, and high production efficiency, and provide a strong, metallurgical bond with the substrate, making them less prone to delamination and suitable for long-term use [7,54].

Due to its exceptional performance, hot-dip aluminum coatings find widespread applications in various industries, including chemical, metallurgical, construction, power, and automotive manufacturing. They are used in chemical plants for heat exchangers and chemical medium transport pipelines, in metallurgy for high-aluminum cooling water pipes and heating furnace heat exchangers, in construction for large buildings' roofs and sidewalls, and chimney flues, in the power industry for overhead communication cables and power lines, and in automotive manufacturing for car floors, cabins, and exhaust systems [55,56]. In the past research, there is a lot of research has been conducted in evaluating hot-dip Zn coating, but some research about hot-dip aluminum is less. Although hot-dip aluminum coating has been proof has a better anti-corrosion ability, the corrosion behavior in the actual atmospheric environment is still less. The corrosion behavior of hot-dip aluminum coating in many kinds of environments should be summarized.

1.4 Organization and outline

The dissertation is divided into seven chapters, including this introduction and the other six chapters. In the introduction part, a review of important research related to hot-dip aluminum coating is provided, outlining the research objectives and summarizing relevant literature.

In chapter 2, To study the application of hot-dip aluminum coating in a marine environment, the research focused on a trestle that had been in service for 28 years on an oil tank. Initially, the corrosion depth of key areas of the trestle was monitored for two years using MSP (Monitoring steel plate) steel plates. Subsequently, core specimens were extracted from locations with significant corrosion depth using actual sampling methods. Microscopic observation and analysis were then employed to assess the corrosion situation. The general patterns of the protective performance of hot-dip aluminum in a marine environment were summarized.

In chapter 3, To gain a more comprehensive understanding of the corrosion behavior of hot-dip aluminum in atmospheric conditions, an eight-year atmospheric exposure experiment was conducted at five locations: Kyoda, University of the Ryukyus, Kyushu University, Momochi, and Tomakomai. Except for Tomakomai, which is located by the seaside, the other sites are within urban areas. This extensive study aimed to investigate the corrosion performance of hot-dip aluminum in urban environments. The primary objective of this research was to study the corrosion resistance of hot-dip aluminum, introducing a comparative analysis with 55Al-Zn and hot-dip Zn coatings. Long-term atmospheric exposure experiments can reveal the practical applications of hot-dip aluminum in actual atmospheric environments. Comparing hot-dip 55Al-Zn and hot-dip Zn allows for a comprehensive assessment of the advantages and disadvantages of aluminum-based coatings and zinc-based coatings in different environments.

In chapter 4, the corrosion behavior of the hot-dip aluminum coated steel plate and the other metal coating coated bolt used in the joints was researched. The metal coatings consist of Zn, 55Al-Zn, and the stainless. Through electrochemical fundamental research, the mechanism of contact corrosion between different metals was investigated. Subsequently, a four-year atmospheric exposure experiment was conducted in two sites one is near the sea and doesn't have the rain washing effect and one is in a place that far

from , providing practical applications for the contact corrosion of different metals.

In chapter 5, The bridge fence and some ancillary facilities often come into contact with concrete. However, due to aluminum being a two-phase oxide, potential corrosion issues in contact with alkaline materials have not been thoroughly researched. This experiment was designed to investigate the interaction between hot-dip aluminum and fresh concrete. The experiment extensively documented the pH changes in fresh concrete and the adhesion conditions at the contact surface between hot-dip aluminum and concrete. For hardened concrete, a two-year atmospheric exposure experiment was conducted at three locations in Kyoda, the University of the Ryukyus, and Kyushu University. The experiment verified the real-world conditions in practical applications.

In chapter 6, this section, an overall summary of the work conducted in this thesis is provided, analyzing what tasks have been accomplished and outlining potential areas for future research.

In the appendix, during the manufacturing process of hot-dip aluminum, steel components are immersed in fully molten aluminum solution, with the temperature of the aluminum solution being above 700 °C. Throughout the immersion process, the temperature can have a certain impact on the mechanical properties of the steel components. A heat-affected zone is also formed on the hot-dip surface. To study the extent of the influence of the heat-affected zone on the mechanical properties of steel components, tensile experiments were conducted to investigate the mechanical properties of steel after hot-dip aluminum treatment.

The flowchart of work in this dissertation is shown in Fig. 1-2.

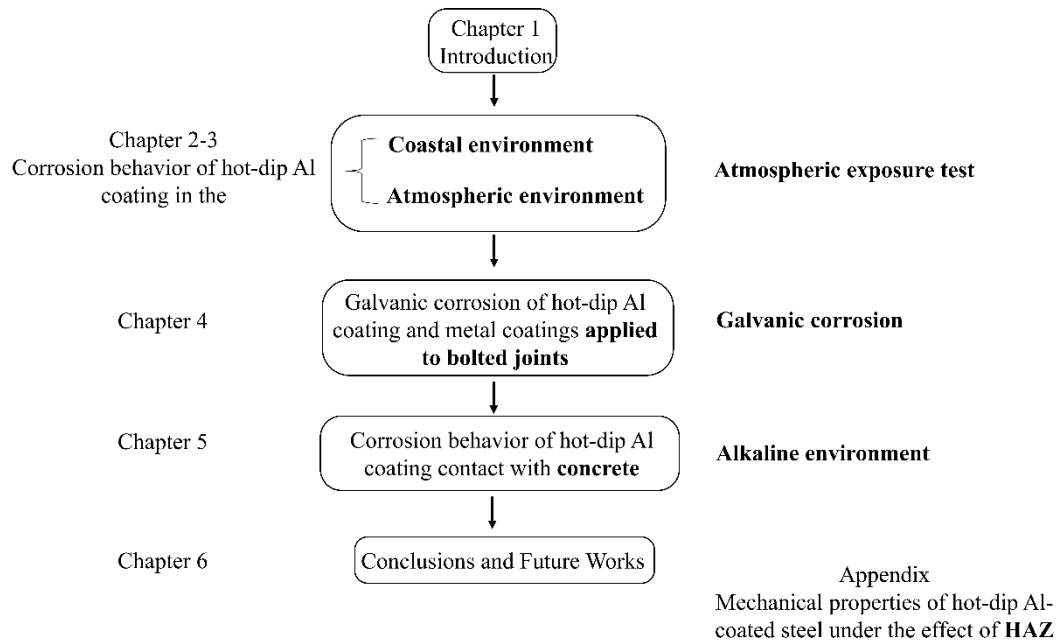


Fig. 1-2 The flowchart of the dissertation.

CHAPTER 2 LONG-TERM CORROSION PROPERTIES OF HOT-DIP ALUMINUM COATING EXPOSURE IN COASTAL ATMOSPHERIC ENVIRONMENT

2.1 Introduction

Steel is the most widely used metallic material for its good mechanical properties and low cost. Much of the steel that is employed in structures is subjected to corrosion due to environmental exposure. The level of carrying capacity and safety of steel structures diminishes with time because of the accumulation of corrosion damage [89,90]. There are many different methods to prevent corrosion such as anodic protection, organic coatings, metallic coatings, and the addition of inhibitor methods that have been applied to the steel structures in order to maintain the corrosion resistance performance in long-term service [91]. In many kinds of metallic coatings, Zinc coatings are extensively used in the steel protection field by the cathodic protection mechanism. Although the life expectancy of hot-dip Zinc coatings has a poor performance in aggressive environments, the coatings are still extensively used in automotive and other industrial applications [29,92]. The reason for the extensive use is the hot-dip Zinc coatings have two-fold protective characteristics. The outmost Zinc layer has a barrier function, it provides a tough, metallurgically bonded coating that completely covers the steel substance and protects the steel from corrosion. Furthermore, the sacrificial action of Zinc coating can protect the steel when defect or discontinuity occurs on its surface [93]. However, due to its sacrificial action, zinc dissolves in the natural environment and pollutes the groundwater circulation system. Moreover, the price of zinc is quite volatile, the price will rise when the usage increases in the future [94,95]. Hot-dip aluminizing is one of the economical methods for the prevention of large tonnages of steel. In commercial, hot-dip aluminum is divided into hot-dip pure aluminum and aluminum-silicon coating categories according to the composition of the molten bath. The pure aluminum coating is used in a place that is resistance to ambient temperature corrosion and the applications demand for high reflectivity surface. Aluminum-silicon coating is used in applications where resistance to

both corrosion and high temperature continuous oxidation. Because a thin and flat intermetallic layer is considered to be a desired microstructures that give the coating layer excellent mechanical properties, silicon is a common element added in the aluminum molten bath [24]. Additionally, the aluminum coating is an alternative to Zinc coating in construction and automobile industries due to its better mechanical properties, excellent high temperature oxidation resistance, and can reduce weight. For these reasons, aluminum-based coatings have gained more attention in recent years [36].

2.2 Experimental

2.2.1 Monitoring steel plate (MSP) assessment

The MSP specimens are square steel plates (JIS G 3106 SM490A) used for environmental monitoring with a dimension of $60 \times 60 \times 3$ mm. The MSPs were degreased by acetone and blasted with abrasive particles before being attached to the trestle. The chemical composition is shown in Table 2-1. The attached position of MSPs specimens in this study is shown in Table 2-2. The core specimens were removed from the trusses of the trestle by a borehole. The cylindrical specimens (JIS G 3101 SS400 diameter: 12mm) were used for electrochemical measurement. The Fe-Al intermetallic coating specimens were used to simulate the situation that which the metallic coating was destroyed or defected by the corrosion medium. Study the corrosion resistance of steel members after metallic coating was dissolved or defective. The area of the specimens that were immersed in the glass cylinder is 489.8 mm^2 . The glass cylinder was filled with NaCl solution. In this electrochemistry test, in order to estimate the corrosion rate, the polarization curve data were used for calculating the instantaneous corrosion rate values i_{corr} through the Stern-Gerry equation.

Table 2-1 Chemical compositions of MSP (wt.%)

C	Si	Mn	P	S	Fe
0.170	0.46	1.46	0.0140	0.005	97.9

	Toward direction	(a)	Land part				Marine part		
		(b)	(c)	(d)	(e)	(f)	(g)	(h)	
MSP	Skyward	✓		✓	✓	✓	✓		
	Groundward	✓	✓	✓	✓	✓	✓	✓	
	North			✓	✓	✓	✓		
	South			✓	✓	✓	✓		

Figure 1 illustrates the dimensions of the heat conduction sheet and the MSP. The front view shows the MSP (60 × 60 × 3t) with a 5 mm gap from the top and left edges. The back view shows the heat conduction sheet (40 × 40 × 1t) with a 15 mm gap from the top and left edges. The cross-sectional view shows the sheet (15 mm thick) and the MSP (40 mm wide) with a 15 mm gap. A double side tape is indicated between the sheet and the MSP. The unit is mm.

13

The trestle coated by hot-dip aluminum coating had been exposed to a coastal atmospheric environment for about 25 years. The trestle is located on the coast of Kagoshima as an oil terminal for oil pipeline transportation. Fig. 2-2 shows the location of the trestle. (Lat. 31°29'N, Long. 130°32'E) The environmental data of the area where the trestle is located is as follows: mean temperature 19°C, average humidity 75%, and average daily precipitation 10.4mm. The attachment method and the direction of MSP specimens are shown in Fig. 2-3. The MSP specimens were attached to the truss and the tilt angle is 30° or 45°. The MSP specimens can attach to skyward, groundward, north, and south four directions. The skyward of MSP specimens has the rain-washing effect, as opposed to this, the groundward direction has nearly no rain-washing effect due to the blocking effect by the skyward. The north and south sides also have the rain-washing effect in a certain owing to the slanting rain. The rain-washing effect can play an important role in cleaning steel structures and reducing the accumulation of flying salt in the marine environment. Fig. 2-4 shows the attachment locations of MSP specimens, the 21 MSP specimens were attached to both land part and marine parts in order to evaluate the corrosion rate in the coastal and marine environments. The outer and inner truss was also attached by MSPs to evaluate the corrosion rate in different parts of the trestle. After one year of exposed to the coastal environment, the MSP specimens were retrieved and used for mean corrosion and rust thickness analysis. The mean corrosion depth was calculated by the mass reduction of MSP specimens before and after exposed. The rust thickness was measured by the electromagnetic film thickness gauge. (The resolution ratio : 1 μm (0~999 μm), 0.01mm (1~10mm)) The average rust thickness was considered to be the average value of 11 points in the middle of MSP specimens. At the beginning of the experiment, observations were made every three months and recorded whether any flaking phenomenon.

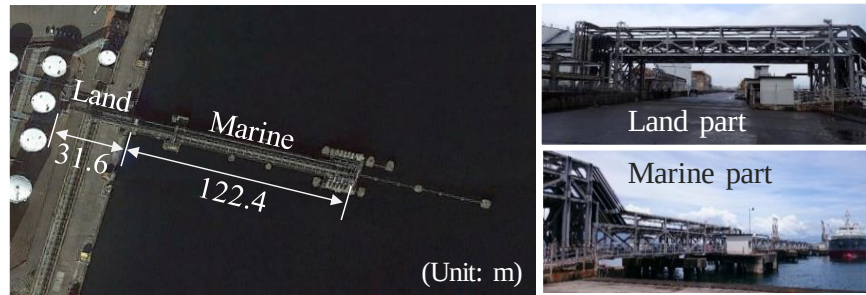


Fig. 2-2 The location and overview of the trestle in Kagoshima oil terminal.

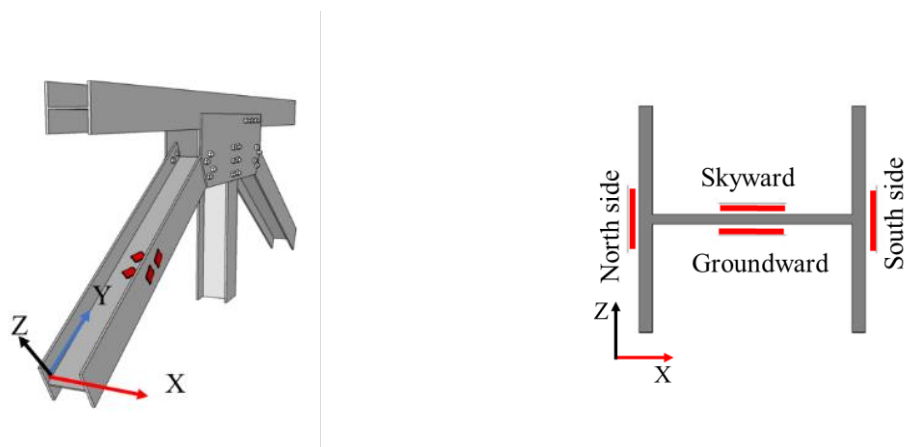


Fig. 2-3 Schematic diagram of the attachment method of MSP specimens.

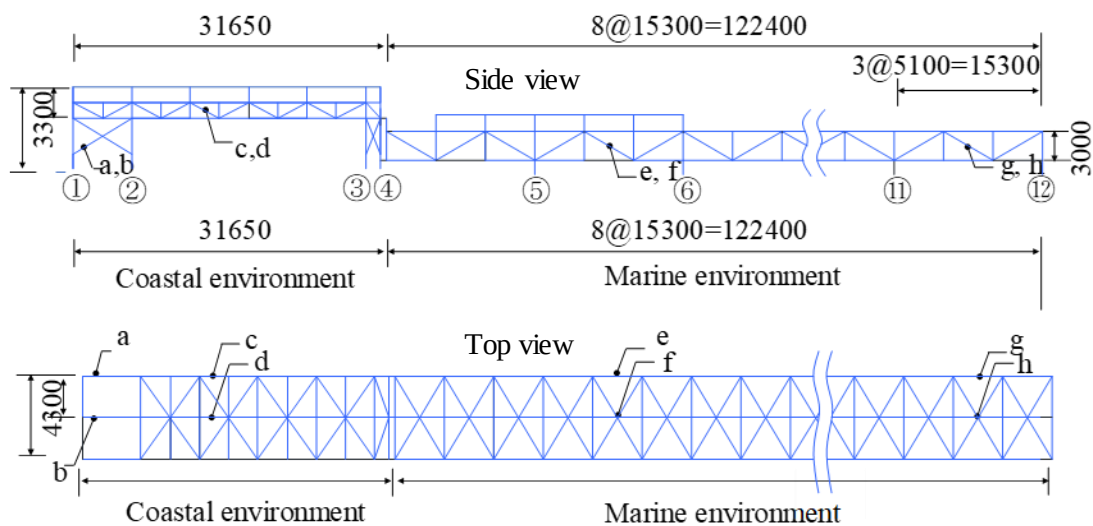


Fig. 2-4 The attachment locations of MSP specimens (unit: mm)

2.2.2 Cross-sectional analysis of core specimens

According to visual inspection and the corrosion depth of MSPs specimens, three locations with different degrees of deterioration are selected as the target area for making the core sample. The core samples were removed from the trestle by the borehole (inner diameter: 25mm). The core specimens were fabricated by embedding the cores in phenolic resin, hardening, and polishing with alumina suspension (particle size: 3 μm). The cross-section of each core specimen was observed by scanning electron microscope (SEM) and the elemental concentration variations was obtained by energy dispersive spectroscopy using SU3500 (Hitachi corporation). In addition, the elemental distribution was obtained by electron probe microanalysis (EPMA) by using EPMA-1600 (Shimadzu corporation).

2.2.3 Electrochemical measurement

The open circuit potential (OCP) and potentiodynamic polarization measurements were performed by using Princeton applied research (AMETK corporation). OCP measurements are recorded with respect to the saturated AgCl electrode. The three-electrode cell was used in polarization measurements. The saturated Ag/AgCl as a reference electrode (RE) and a platinum sheet was used as the counter electrode (CE). The anodic and cathodic polarization curves were obtained by scanning the potential at the rate of 0.33 mV/s. The electrolyte is the four concentrations of NaCl aqueous neutral solution. (0.1, 3.5, 10, 26.4wt.%) The temperature of the measurement environment is about $22\pm 2^\circ\text{C}$, with the NaCl electrolyte at rest without any external stirring [96,97].

2.3 Results

2.3.1 The environment assessment by MSPs

The corrosion depth of MSPs after one-year exposure, as shown in Fig. 2-5. As presented in Fig. 2-5 (a,c,d,e), in the same position, the corrosion depth of groundward is much more than that of skyward. The MSP specimens attached in two lateral surfaces of each beam in the structure were noted as 'North' and 'South', the corrosion depth of the two different towards is not much difference. Compared with the rust thickness, the corrosion depth is a better evaluation factor for corrosion degree, because the rusts may

be detached from the MSPs and cause deviations in measurement. Position (a) has the maximum corrosion depth in all MSPs specimens. Accordingly, the groundward of position (a) is a target area to describe the most serious position of the trestle. Conversely, the skyward position (b) is the most complete surface due to visual observation. The skyward of position (b) is used for the most complete part. In addition, the groundward of position (b) is the median of corrosion depth, used to describe the stage of the corrosion process. The skyward of position (a), skyward and ground of position (b) are removed from the trusses of the trestle and made the core specimens in order to study the corrosion process and mechanism of hot-dip aluminum coating.

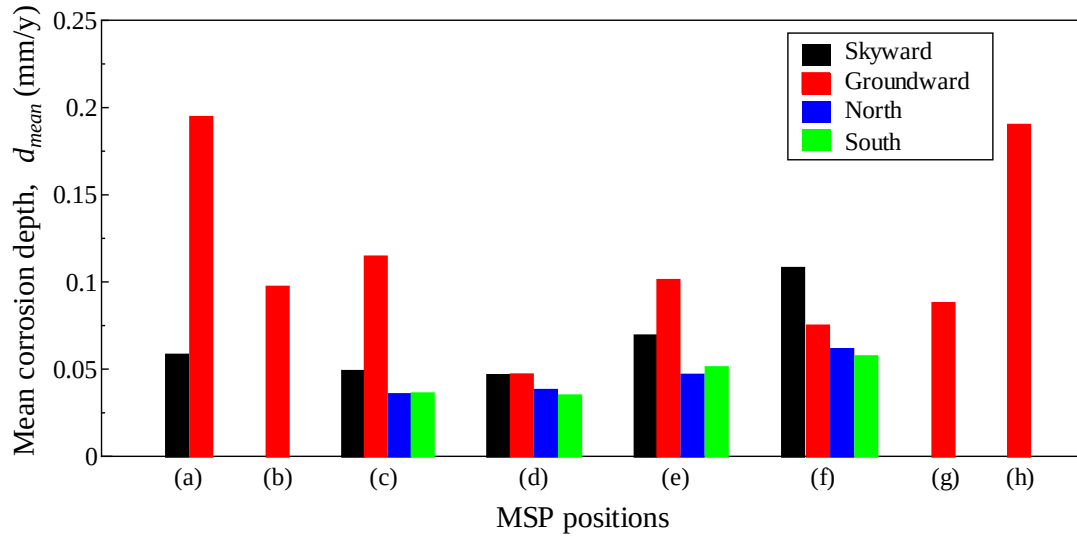


Fig. 2-5 The mean corrosion depth of MSP specimens.

The rust thickness of MSPs is presented in Fig. 2-6. Similar results can be obtained with the corrosion depth. According to the rust thickness of MSPs, Fig.2-5 (a, c, d, e,f) shows the rust thickness of groundward is much higher than that of skyward. Compare the rust thickness of the north and south directions in Fig. 2-5 (c,d,e,f). There is not much difference in the north and south directions. As a consequence, the corrosion depth and rust thickness of groundward and skyward, groundward is much higher than that of the skyward due to the groundward is no rain-washing effect, thus, the salt flying from the marine atmospheric environment accumulated in the ground ward.

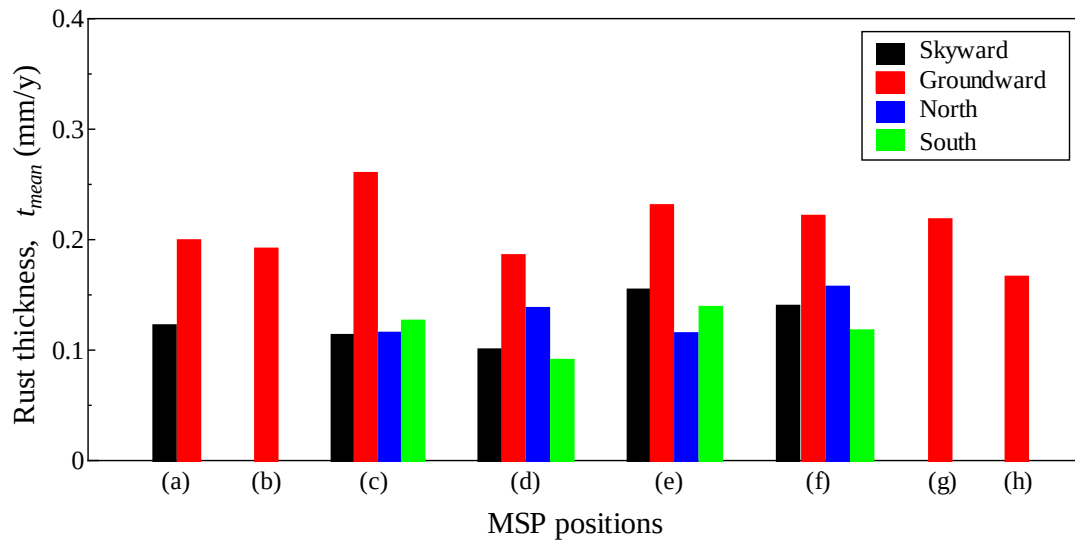


Fig. 2-6 The rust thickness of MSP specimens.

The mean corrosion depth and rust thickness of groundward MSPs according to the distance from the coastal line are shown in Fig.2-5 and Fig. 2-6. The positions a, c, e, g are on the outer trusses, and the b,d,e,f are on the inner trusses. From the trend of change, the corrosion depth and rust thickness of the MSPs specimens on the outer truss are much higher than that of the inner truss. The corrosion depth of point (h) is different from this trendy, the reason could be speculated from several aspects, largest possibility is that the rainwater accumulation functions accelerated the corrosion there.

2.3.2 Backscattered electron image (BSE) and EPMA analysis

Backscattered electron images of the core specimens and the elemental distribution obtained by EPMA analysis on the cross-section perpendicular to the coating surface are shown in Fig. 2-7. In order to obtain the stratification of each metallic layer more clearly and avoid the influence of other impurities, use the polishing with alumina suspension. In this process, the corrosion substance and soluble salts such as chlorides and sub-plates are washed away. From visual inspection, some white corrosion produced on the surface of the skyward position (b) can be observed, this area is the most intact part of the whole trestle. The skyward of position (b) is shown in Fig. 2-7(a), BSE images and EPMA on the cross-section analysis suggest that the outermost aluminum layer is still complete after 25 years of exposure. The coating layer composed of the Fe-Al intermetallic layer and Aluminum layer is mainly intact and without eroding. The concentration of aluminum in

the outermost layer is still high compared with the Fe-Al intermetallic layer. Fig. 2-7 (b) shows the groundward of position (b). From the distribution and concentration of elements Fe and Al, the concentration of Aluminum in the outermost aluminum layer is less than that of in Fe-Al intermetallic layer. This indicates that all of the Aluminum layer starts the dissolve phenomenon, the concentration of aluminum shows the outmost layer has a low concentration of aluminum compared with the Fe-Al intermetallic layer. Distributions of the elements Cl and Mg were detected contain in the outmost aluminum layer. These elements are considered to be derived from the marine environment. It is well known that seawater contains NaCl, Na₂SO₄, CaCl₂, KCl, NaHCO₃, KBr, MgCl₂, MgSO₄, and CaSO₄ [36,98]. Hence, the presence of Mg²⁺ and Cl⁻ indicated that the seawater has penetrated through the outermost aluminum layer. The outermost aluminum layer is mainly in the form of AlCl₃ compounds due to the distribution of elements Al and Cl. Some cracks appeared in the outmost aluminum layer and all of that extend to the Fe-Al intermetallic layer. The position where the cracks cut through the outmost aluminum layer to the Fe-Al intermetallic layer exists, the dissolution and corrosion of the Fe-Al intermetallic layer occur there. The concentration of element oxygen indicates that the outermost aluminum layer is totally deterioration and oxidized. There is a slight dissolution that occurs in the Fe-Al intermetallic layer where the cracks penetrated. The majority of the Fe-Al intermetallic layer is almost completely continuous and provides a lasting cathodic and shielding protection. In general, the corrosion behavior of groundward is more serious than that of skyward in the same position, because there is no rain-washing effect in groundward and it can cause salt deposition more easily. Position (a) is the part where the corrosion deterioration is most severe in the trestle by the MSPs monitoring. Accordingly, it is speculated that the groundward of position (a) is the most deteriorated part of this trestle. Fig. 2-7 (c) shows the groundward of position (a), the outermost aluminum layer completely deteriorated. The majority of the Fe-Al intermetallic layer was deteriorated and only a few areas have the residual intermetallic layer. Both the outermost aluminum layer and the Fe-Al intermetallic layer were heavily oxidized and degraded. From the distribution of elements Mg and Ca, it was speculated that the insoluble substances of magnesium and calcium were deposited in the intermetallic layer. Furthermore, the present of Ca and Mg shows the corrosion

environment has penetrated through the Fe-Al intermetallic layer, the outermost aluminum layer has been completely deteriorated and lost the sacrificial anode action and even the shielding effect[3,7].

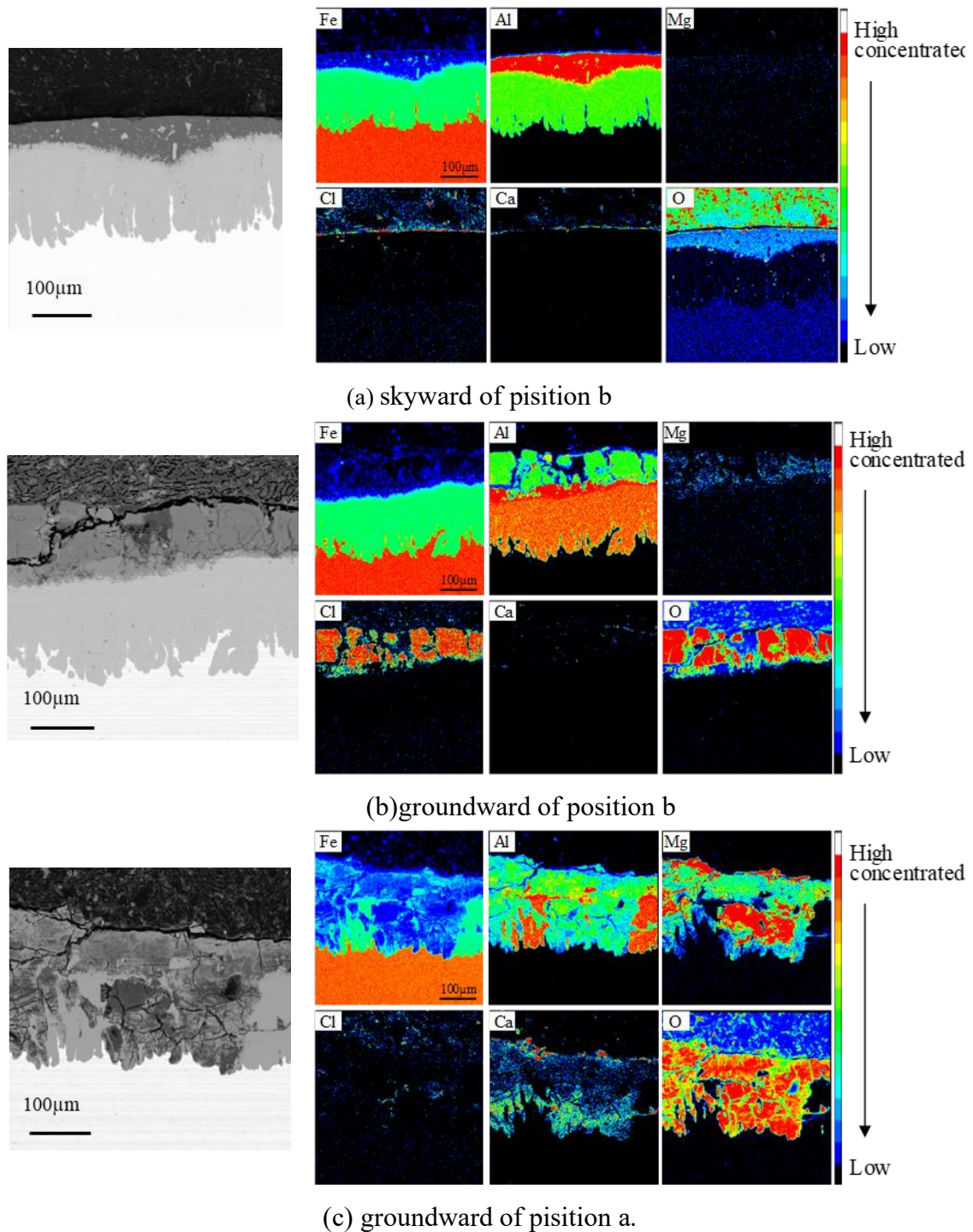


Fig. 2-7. BSE images of core specimens and the element distribution obtained by EPMA on the cross-section.

2.3.3 Electrochemical properties of hot-dip aluminum coating

Fig. 2-8 shows the OCP of pure aluminum and Fe-Al intermetallic layer after immersion in four concentrations of NaCl solution. The potential fluctuations were observed due to the transient process. The oxide layer film is generally porous and the Cl^- ions penetrate through the oxide film and then cause the local breakdown of the passive film, as a consequence, the initiation of pits appears on the passive film. Some pits can be passivated and the others will give the formation of AlCl_4^- complexes [99]. On the other hand, compared with the aluminum layer, the Fe-Al intermetallic affects the behavior of the passive aluminum electrode, and the content of Fe exhibits more electropositive than that of the aluminum layer. The OCP of the Fe-Al intermetallic layer is also more stable than the aluminum layer.

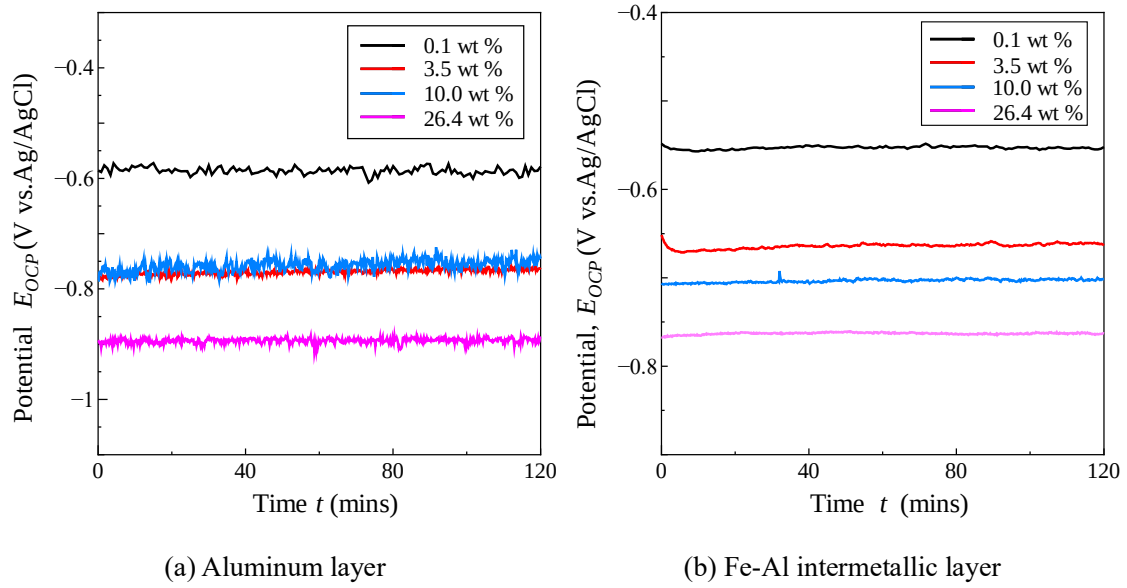


Fig. 2-8 OCP of aluminum layer and Fe-Al intermetallic layer

The potentiodynamic polarization curves results of Al and Fe-Al intermetallic that after 2 hours immersion in four different concentrations of NaCl solution shown in Table 2-3. The scanning speed was 0.33mVs^{-1} . During the test progress, the hydrogen bubbles formation can be observed on the working electrode, following this behavior, the aluminum began to dissolve. The Al_2O_3 film is not stable in water and will more easily become $\text{Al}(\text{OH})_3$ by the hydration. Furthermore, the accumulation of dissolution products of the Al_2O_3 and hydroxide on the electrode surface slows down the rate of aluminum dissolution and H_2 release. In addition, the passive of aluminum in the chloride

environment can be breakdown by the Cl^- interaction between the OH^- of $\text{Al}(\text{OH})_3$, and generate the AlCl_3 at last. The passivation phenomenon is due to the various protective compounds and corrosion products on the surface of specimens [18,19,20]. The aluminum and Fe-Al intermetallic do not cause the passivation phenomenon due to the Al_2O_3 film being dissolved and not many corrosion products on the surface of specimens, as well as, the immersion time being too short and not causing much corrosion behavior[21]. As a result, hot-dip coating contact with the corrosion medium, when the coating layer is dissolved by the corrosion medium. The intermetallic compound layer also has a good corrosion resistance performance, also can play a protective role in corrosion resistance. In corrosion medium, hot-dip Al coating has a good corrosion resistance performance when the surface of the coating is perfect without damaged. The Fe-Al intermetallic compound layer also has a good corrosion resistance performance, when the outer hot-dip coating layer is dissolved by the corrosion medium.

Table 2-3 Corrosion potential E_{corr} (V vs.Ag/AgCl) and corrosion current density i_{corr} (A/cm²)

Concentration of NaCl aq (wt%)	Al layer of coating		Al-Fe alloy layer of coating	
	E_{corr} (mV)	i_{corr} (μA)	E_{corr} (mV)	i_{corr} (μA)
0.10	-583	1.53	-488	2.45
3.50	-755	14.0	-644	11.0
26.4	-880	0.40	-815	0.87

2.4 Deterioration mechanism of hot-dip Al coating

The aluminum layer consists of the outermost aluminum layer and the inner Fe-Al intermetallic layer. The aluminum coating used in this trestle, the thickness of the entire and intermetallic coating is respectively about 50 μm and 80 μm . The interface of the Fe-Al intermetallic layer and steel substance shows a tongue-like morphology due to the iron from the steel substance dissolved into the molten aluminum bath [23]. Nevertheless, the interface of the intermetallic layer and aluminum layer is very smooth compared with the steel substance [37]. The phase distribution diagram of the hot-dip aluminum coating is shown in Fig. 2-9. The outermost layer is the aluminum coating layer, the thickness of this layer is about 30 μm . The FeAl_3 disperses in the interface of the aluminum coating layer and intermetallic layer. The majority of the Fe-Al intermetallic layer is composed of Fe_2Al_5 . The trestle of oil terminal coated by hot-dip aluminum coating in Kagoshima has been used for 25 years. The skyward position (b) has the most completely appearance

from the visual observation, was selected to elements analysis by the EDS. The backscattered electron image and depth profiling of elements on the cross-section along the horizontal direction were obtained by SEM-EDS shown in Fig. 2-10. The target area is a rectangular region ($240\text{ }\mu\text{m}\times 22\text{ }\mu\text{m}$), the points were obtained per $5\text{ }\mu\text{m}$ along the directions from the steel substance to the outermost aluminum layer, the elements analysis was totally calculated by weight percent. The compositional change in the weight percent concentration of iron, aluminum, carbon, silicon, oxygen through the cross-section indicated that the existence of more than one phase and the features of each layer were also obvious. Moreover, the depth profiling of the elements showed that the Fe_2Al_5 and FeAl_3 were not eroded by the marine environment due to the outermost aluminum layer being almost completely. Accordingly, for most of the trestle especially the skyward part, the performance of the hot-dip aluminum layer is perfect and was not corroded by the severe environment. The groundward of position (a) is the most serious corroded part by the vision observation and MSPs monitoring. Hence, using the EDS for a semi-qualitative assessment of the most corroded part, the service life of the whole aluminum coating can be inferred. Fig. 2-11 shows the depth profiling of the elements consisting of hot-dip aluminum coating in the groundward position (a). The results indicate that the outermost aluminum, FeAl_3 , and a part of Fe_2Al_5 layers were dissolved and some oxidation materials existed in the outermost layer, however, there are about $20\text{ }\mu\text{m}$ of Fe_2Al_5 layer existence [37]. In consequence, the Fe_2Al_5 layer still exists and can protect the steel substance from corrosion. In a word, even though the most corrosive part, the steel substance is still complete after being exposed to the coastal atmospheric environment for 25 years.

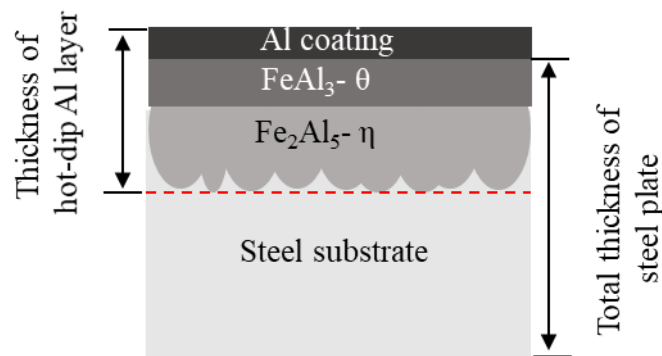


Fig. 2-9 Schematics showing the thickness of aluminum layer, Fe-Al intermetallic layer, steel substance

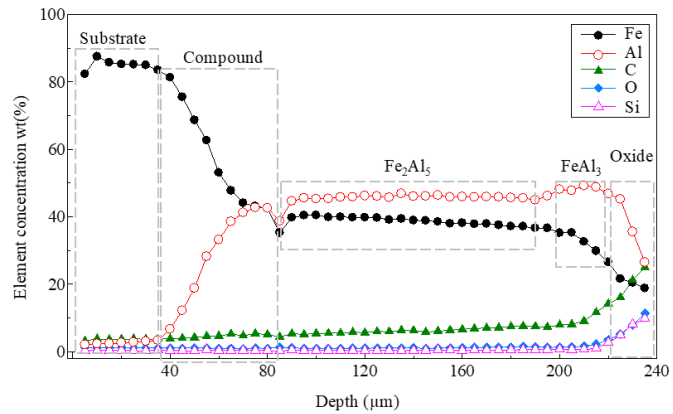
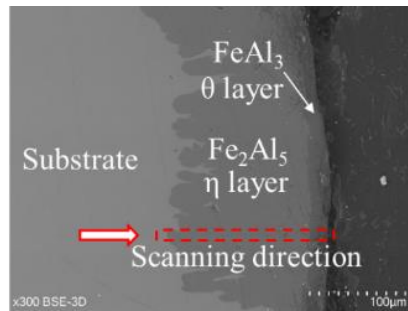


Fig. 2-10 Cross-sectional micrograph and EDS analysis of core specimen get from Kagoshima trestle

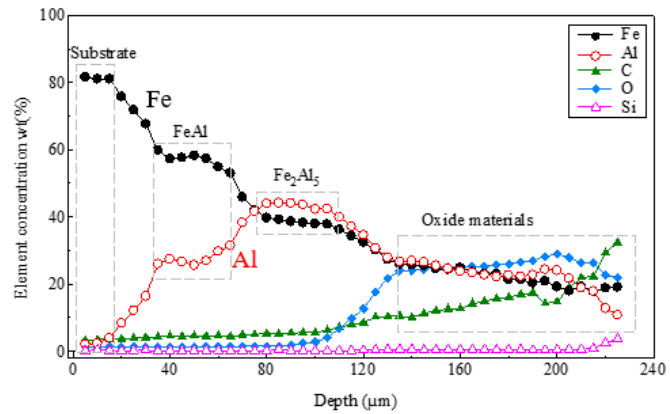
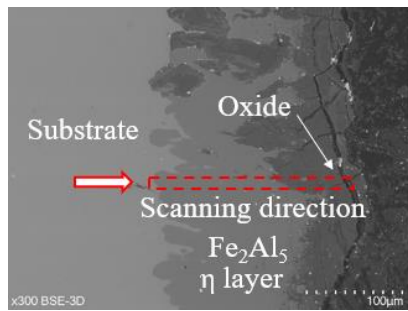


Fig. 2-11. Cross-sectional micrograph and EDS analysis of core specimen get from Kagoshima trestle.

Pitting corrosion is a common corrosion morphology in steel structures coated by hot-dip aluminum coating near the coastal atmospheric environment [13]. At the beginning of the aluminum coating service, the surface of the aluminum coating was completely covered with the passive film. In the corrosive environment, the passive layer is cracked after the progress of adsorption and penetration of Cl^- through the oxide film, the steel substance is still protected except for several small paths. Afterward, the aluminum layer is in contact with the corrosive environment by the cracks of the passive film. Furthermore, the dissolution of the aluminum layer begins, the requirement of pitting corrosion is met and the passivation behavior does not occur anymore, the pitting begins to grow. The aluminum layer begins to grow and the pitting hole becomes more and more depth. The pitting grow depth is related to the conductivity of the bulk electrolyte. In general, the pitting depth and pitting current density are related to time, the pitting depth is

proportional to $t^{1/3}$ and the current density is approximately $t^{1/2}$. [100–103]. Moreover, the aluminum layer begins the pitting corrosion, the small holes occur on the surface of the aluminum layer. With the growth of corrosion further, the pitting depth increases with time. The development direction of pitting corrosion is downward towards the Fe-Al intermetallic layer and proceeds towards both sides. In this way, the direction of corrosion development is a rapid rate of downward extension and slow erosion to both sides. In addition, the aluminum layer also causes dissolution and deterioration as a whole, and the cracks that are due to the pitting corrosion become more and more widening. As the whole aluminum layer deteriorates, the cracks extending to the Fe-Al intermetallic layer also cause deterioration and dissolution at the boundary of pure aluminum and Fe₂Al₅ phase [37–39]. As the corrosion continues, the element concentration of aluminum in the outermost layer (pure aluminum layer) is significantly less than that of the Fe-Al intermetallic layer, furthermore, the corrosion and deterioration of the aluminum layer begin at each crack to the surrounding, and then spread to the entire aluminum layer. More specially, after all of the aluminum layer has deteriorated and oxidized, the deterioration of Fe-Al intermetallic gradually continues and spreads. Similarly, the cracks develop and continue to downward and on the two sides, the corrosion behavior of the Fe-Al intermetallic layer is different from that of the aluminum layer. With the corrosion progress of the aluminum layer, the bottom of the cracks (outermost surface of Fe-Al intermetallic layer) causes the corrosion behavior due to the effect of pitting corrosion continuing along with the downward direction. The corrosion behavior of the Fe-Al intermetallic layer, the pitting corrosion, and cracks that occur in the Fe-Al intermetallic layer are similar to the aluminum layer, whereas, according to the distribution of element iron obtained by EPMA, there is no corrosion phenomenon observed in the steel substance. Accordingly, the conclusion can be drawn that the outermost aluminum layer and Fe-Al intermetallic layer are sacrificially dissolving to protect the steel substance from corrosion, the electrochemical test also supports this view. Fig. 2–12 shows the OCP of the aluminum layer, Fe-Al intermetallic layer, and steel substance. In addition, the E_{OCP} of three different layers in four concentrations of NaCl solutions, the OCP sequence of them is steel substance > Fe-Al intermetallic layer > aluminum layer [104,105]. In the other world, when the cracks reach the surface of the steel substance, the Fe-Al intermetallic and steel substance all show the cathodic current. Furthermore, the aluminum layer and Fe-Al intermetallic layer prove that the coating layer will corrode preferentially and consequently will protect the steel substance from corrosion. In this case, it is speculated that all the aluminum layer and Fe-Al intermetallic layer are deteriorated, and the steel substance begins to cause corrosion phenomenon. The

element's distribution of Mg and Ca also indicates that the seawater has penetrated through the Fe-Al intermetallic and porous corrosion products, but the steel substance cannot obtain these elements also indicates that the corrosion is still not immerated into the steel substrate. After 25 years of exposure to the coastal environment, the steel structures of the trestle are still in good condition by using of hot-dip aluminum coating. The schematic stages of hot-dip aluminum coating in the corrosion process are shown in Fig. 2-13. The corrosion process and its morphology were summarized from a large number of observations at different locations by BSE image. In brief, pitting corrosion on the surface of the aluminum coating layer causes cracks, many cracks continue to progress and spread, even then extend to the Fe-Al intermetallic layer and corrode slowly on both sides. Corrosion occurs preferentially at the junction of cracks and the Fe-Al intermetallic layer, the corrosion behavior of cracks is similar to the process of occurs in the aluminum layer. The corrosion process continues, and the Fe-Al intermetallic layer continuously deteriorates, the steel substance is still completely and without any corrosion phenomenon due to the cathodic protection provided by the residual Fe-Al intermetallic layer [106,107]. It is speculated that the corrosion process is further intensified and all of the Fe-Al intermetallic layers deteriorated, even disappearing. The steel substance will no longer have sacrificial anodes for protection, the corrosion phenomenon will occur on the steel substance. Moreover, the groundward of the outer trusses and the other parts where the corrosion behavior is serious will deteriorate in the coastal environment and reduce the bearing capacity of this trestle.

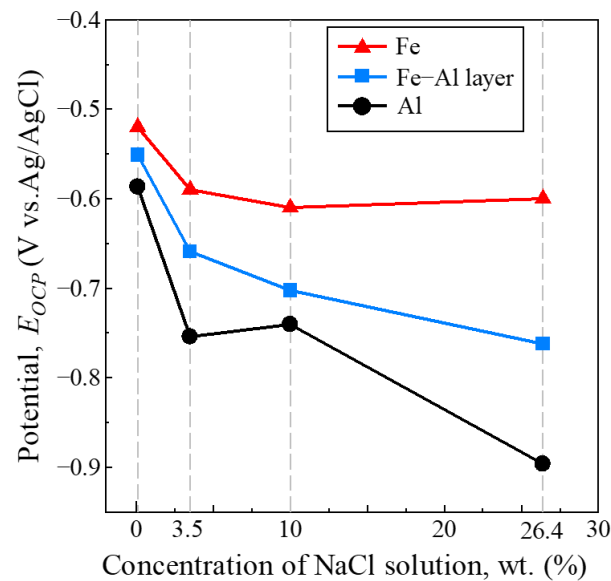
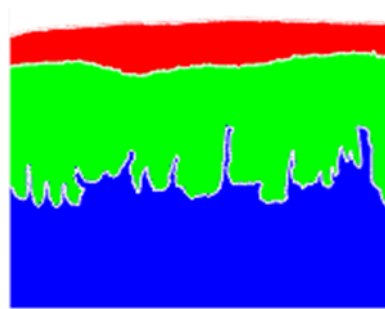
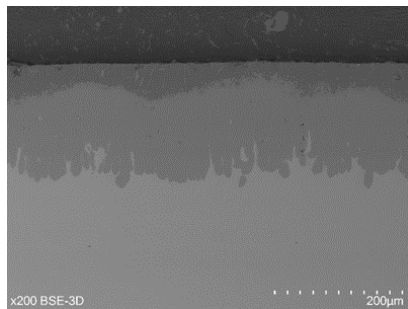
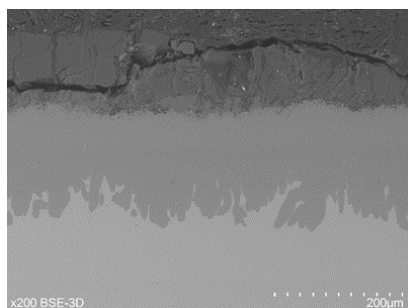


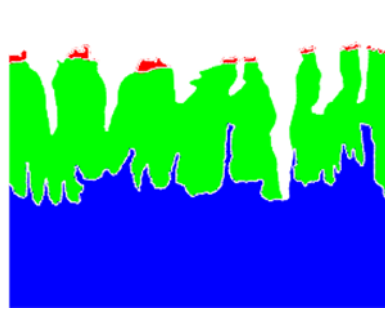
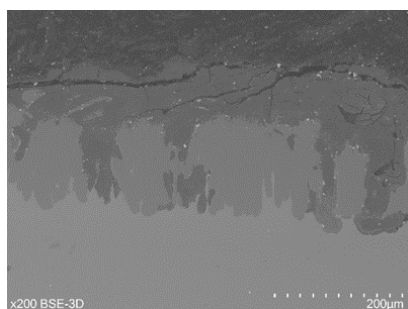
Fig. 2-12. Open circuit potential of aluminum, Al-Fe intermetallic, Fe specimens in four concentrations of NaCl solution



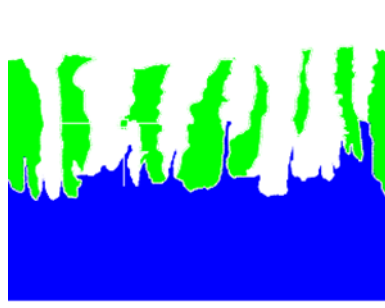
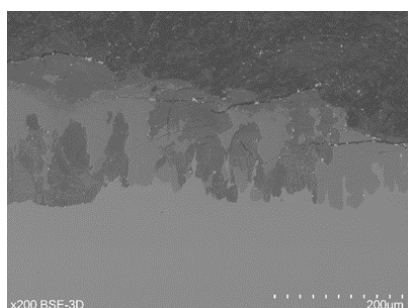
Step 1:The aluminum layer is completely



Step 2:The cracks occurs and extend to the Fe-Al intermetallic layer



Step 3:The aluminum layer dissolved and the creaks continues through to Fe-Al intermetallic layer



Step 4:The Fe-Al intermetallic layer dissolved, the steel substance still completely

Fig. 2-13 The BSE image and schematic diagram of corrosion process.

2.5 Summary

The corrosion behavior of hot-dip aluminum coating of long-term exposure on a coastal atmospheric environment for about 25 years was studied through micro observation, elements analysis, and electrochemical test. The following conclusions can be drawn:

- (1) In the long-term coastal environment, hot-dip aluminum coating has a significant shielding effect due to the thin oxide film on the surface of the coating.
- (2) The steel substance can be protected by the aluminum coating due to sacrificial anode protection. Both the aluminum layer and the Fe-Al intermetallic layer can protect the steel substance.
- (3) The deterioration process of the aluminum coating layer and Fe-Al intermetallic layer is similar, the cracks occur and extend to the inner layer and, at the same time keep expanding to both sides.
- (4) The steel substance has no corrosion behavior that can be observed until the Fe-Al intermetallic layer is almost dissolved.

CHAPTER 3 ATMOSPHERIC EXPOSURE TEST OF HOT-DIP ALUMINUM COATING

3.1 Introduction

The harm of corrosion is immense. Atmospheric corrosion is a significant factor leading to early failure and damage of products, equipment, devices, structural components, and more. While atmospheric exposure tests are realistic and accurate, the experimental cycles are often lengthy. According to statistics, economic losses due to atmospheric corrosion for metal materials account for over 50% of the total corrosion losses. Additionally, the environmental damage caused by atmospheric corrosion is also substantial. In the marine atmospheric environment, the presence of a large amount of Cl⁻ in the atmosphere exacerbates metal corrosion, potentially resulting in severe consequences once metals corrode. Several developed industrialized countries recognized the serious hazards of corrosion early on and initiated research efforts. As early as the early 20th century, the American Society of Testing Materials (ASTM) began establishing atmospheric corrosion exposure sites in different environments, conducting extensive and fundamental atmospheric exposure tests on various materials, including metals (such as steel and light metals), coatings, and protective layers [54,125,126]. The United States pioneered the establishment of a network of natural atmospheric environment corrosion test stations, systematically and comprehensively accumulating corrosion data.

Following the American Society of Testing Materials, in 1930, the British Iron and Steel Research Association (BISRA) also commenced atmospheric exposure tests on various types of steel [35,127]. In 1934, BISRA specifically set up the Atmospheric Corrosion Committee and established an atmospheric corrosion network. Subsequently, in 1946, the Soviet Academy of Sciences initiated the formation of the first batch of eight atmospheric exposure test stations. In 1966, the Soviet Academy of Sciences organized member countries to jointly formulate a 20-year collaborative atmospheric corrosion test plan concerning protective layers and metals [128]. In the 1950s, Japan also established multiple atmospheric corrosion test stations. Currently, countries worldwide continue to increase investment and delve deeper into atmospheric corrosion research. This has

intensified international collaboration in corrosion research, evolving from simple data accumulation to comprehensive and in-depth studies covering various aspects of corrosion mechanisms. The establishment of corrosion grades, corrosion mathematical models, and research on corrosion laws has standardized research, increased the universality of corrosion data, and multinational collaborative atmospheric corrosion experiments and research have gradually become a current development trend.

3.2 Experimental

To assess the durability and corrosion performance of the hot-dip aluminum-coated film, atmospheric exposure tests were conducted on specimens with cross-cut patterns. The external dimensions and patterns of the specimens are shown in the diagram, with the cross-cut configuration specially designed to study the influence between embedded wire locations. Ensuring consistency in the processing of all specimens was particularly important during the experimental setup. The Yamazaki Mazak machine tool was used for specimen processing, employing a Nine9-V060-2032 cutter produced by Tool de International Co., Ltd. The cutter's opening angle was set at 60 degrees, with a rotation speed of 9600 revolutions per minute and a movement speed of 100 mm per minute. It was crucial to ensure that the blade penetrated the steel substrate by at least 100 micrometers during the cutting process. This was done to validate the sacrificial anode performance of the metal coating in atmospheric corrosion. The schematic diagram of the specimens processing is shown in Fig. 3-1. The hold of near the edge is used for the hot-dip process, all steel structures are immersed into the metal coating solution during hot-dip coating process. Therefore, on the part of the steel structure, positions need to be reserved for the insertion of steel cables. In this specimen the diameter of the holes is 8 millimeters. The defect part of the cross-cut is shown in Fig. 3-2. The width of the embedded cross-cut section in the specimen is 0.2 mm, and the depth of embedding into the steel substrate is generally ensured to be between 100 to 160 μm . This ensures that the embedded section is exposed to study the sacrificial anode effect of hot-dip aluminum in the atmospheric environment after experiencing mechanical scratches.

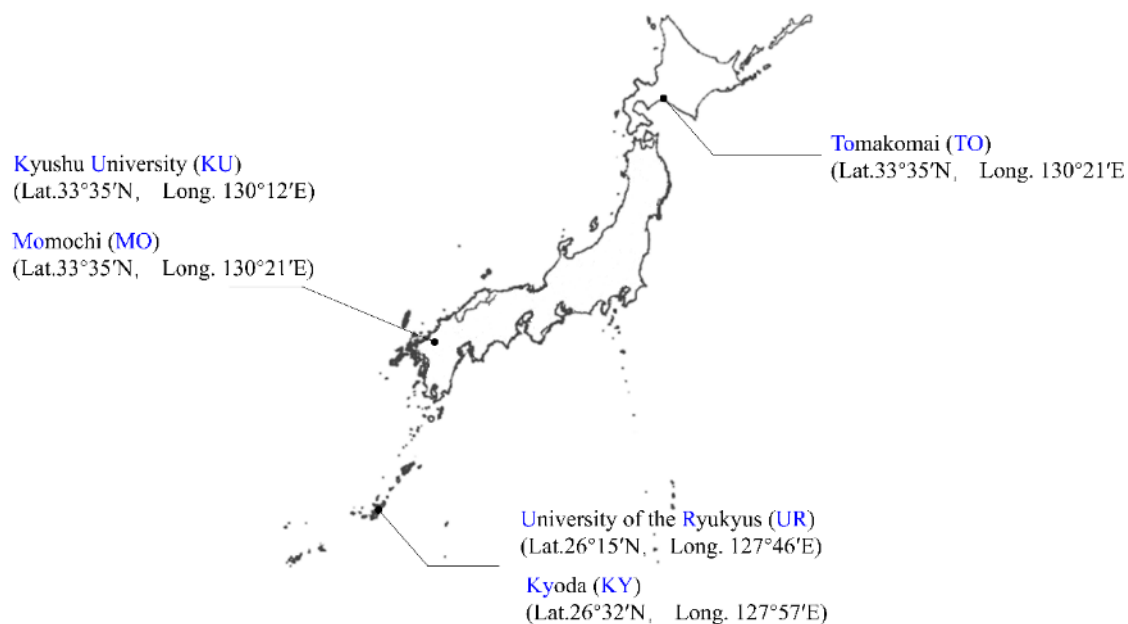


Fig. 3-3 The location of exposure sites.

Table 3-1: The atmospheric data of the exposure sites.

Exposure site	Temperature <i>T</i> (°C)	Humidity <i>RH</i> (%)	Airborne salt <i>w</i> (mdd)	Average precipitation (mm/day)	Offshore distance (m)	Rain washing effect
KY	22.5	83.5	0.5	5.3	30.0	Without
UR	23.0	81.9	0.3	5.2	2,300	With
KU	17.3	76.9	0.5	6.2	2,900	With
Mo	18.7	71.4	0.6	4.9	50.0	Without
To	7.4	78.9	2.4	3.6	2.0	With

The atmospheric exposure experiments were conducted at five different test sites. The location of the exposure sites is shown in Fig. 3-3. The general information of atmospheric exposure sites can be briefly stated below: 1) The specimens at the University of the Ryukyus (denoted as UR) were placed at the Chihara campus, approximately 2,300 meters from the east coast of Okinawa Main Island, exposed to the open air with rain washing effects. 2) Kyoda (denoted as KY) is situated just 30 meters from the west coast of Okinawa Main Island. The exposure site is located under the

overpass of the Okinawa



(a) University of the Ryukyus



(b) Kyoda



(c) Kyushu University



(d) Momochi



(e) Tomakomai

Fig. 3-4 Photographs of the atmospheric exposure test sites.

Expressway. Due to the lack of rain washing effects, high salt accumulation is common in this area. 3) The exposure site at Kyushu University's (denoted as KU) Ito campus is located approximately 2,500 meters from the coastline, exposed to the open air with rain washing effects. 4) The exposure site in Momochi (denoted as Mo) is situated about 70 meters from the coastline of Hakata Bay, beneath the elevated bridge of the Fukuoka Kitakyushu Expressway. This location experiences strong wind forces. 4) Finally, the atmospheric exposure site in Tomakomai City (denoted as To), Hokkaido, is situated

about 2 meters from the coastline. Due to its proximity to the coastline, there is a higher concentration of airborne sea salt. The exposure is open to the air with rain washing effects. The detailed atmospheric data are shown in Table 3-1. The appearance of the specimens in different atmospheric exposure test sites is shown in Fig. 3-4. The basic arrangement of the specimens during the exposure test can be marked.

3.3 The surface condition of the specimens after the atmospheric exposure test.

For the atmospheric exposure test, five different test sites KY, UR, KY, Mo, and To were selected. The exposure sites in KY and Mo are located below the bridge of the highway, shielding the effect of bridges and structures. Additionally, these two test sites are 30 meters and 50 meters away from the coastal, respectively. Due to their proximity to the coast, a large amount of airborne salt is expected to adhere to the surfaces of the test specimens. The atmospheric exposure site in To is only 2 meters away from the ocean, making it the closest to the coastal. Therefore, the amount of airborne salt is expected to be the highest, but the absence of buildings allows for rain washing effect. The atmospheric exposure sites at KU and UR are more than 2 kilometers away from the coastline but still experience rain washing effect.

The main purpose of this experiment is to study the corrosion resistance of hot-dip aluminum in various atmospheric environments. For comparison, hot-dip 55Al-Zn and hot-dip Zn coatings were also included. The surface characteristics of the test specimens after the atmospheric exposure experiment are presented in Fig. 3-5. Analysis of the surface properties of hot-dip aluminum reveals its excellent corrosion resistance in atmospheric environments. The test specimens at KU, UR, and To show a clean and intact surface with no signs of corrosion. Even in the cross-cut positions where corrosion is most likely to occur, no severe corrosion behavior was observed. In the exposure sites with rain washing effect, rainwater washes away the deposited chloride and sulfide on the surface of the test specimens [129–131]. The upper surface of the test specimen is where rainwater can wash most effectively, and essentially no corrosion was observed. While the chances of contact with rainwater are relatively less for the lower surface compared to the upper surface, during rainfall, wind-induced tilting can cause rainwater to reach the lower surface. As rain washing effect is possible for both skyward and groundward

surfaces in the KU, UR, and To test sites, the surface condition of the test specimens remains good.

Comparison of areas without rain washing effect, such as KY and Mo test sites, reveals the accumulation of airborne sea salt due to the absence of rain washing effect. Airborne salt continuously accumulates in these two exposure sites, leading to a gradual worsening of the corrosion degradation on the surface of the test specimens. When comparing skyward and groundward orientations, the skyward direction, being more prone to salt accumulation, shows relatively more pronounced degradation. Although groundward degradation is not as severe as skyward, it is still noticeably worse compared to other atmospheric exposure sites with rain washing effect. When comparing the test specimens from the KY and Mo atmospheric exposure sites, the deterioration of KY test specimens is relatively more severe. The distances from the coastline for KY and Mo are 30 meters and 50 meters, respectively, with roughly equivalent airborne salt content. However, the average temperature and relative humidity at the KY exposure site are higher, creating a harsher corrosion environment with higher temperature and humidity. Compared to KY, the corrosion area of hot-dip aluminum at the Mo exposure site is significantly smaller. The corrosion of hot-dip aluminum is primarily overall degradation, with no significant differences observed between cross-cut sections and regular areas. After the initiation of corrosion in the embedded sections, the spreading of corrosion is not very noticeable. In environments with high chloride ions, aluminum surfaces are prone to localized pitting corrosion, which can manifest in various corrosion patterns. Near the initiation of pitting, corrosion begins to accelerate significantly. The yellow-brown substance represents corrosion that extends beyond the outermost aluminum layer, progressing into the Fe-Al alloy layer. The yellow-brown substance consists of corrosion products of iron elements in the alloy layer reacting with the atmospheric environment. Comparing the test specimens of hot-dip aluminum and 55Al-Zn reveals that, for the atmospheric exposure sites with rain washing effect (UR, KU, To), the surface condition of hot-dip aluminum specimens is significantly better than that of 55Al-Zn specimens. The surface of hot-dip aluminum remains smooth and intact. In the To atmospheric exposure site, both types of specimens show a decrease in glossiness and an increase in roughness for the 55Al-Zn specimens. This indicates that in high-salt environments, as



Al coating

55Al-Zn

Skyward

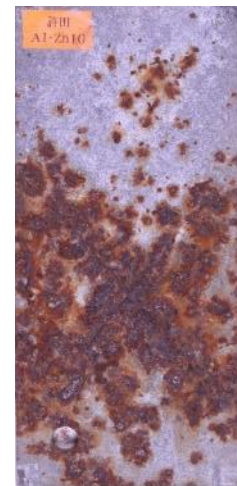
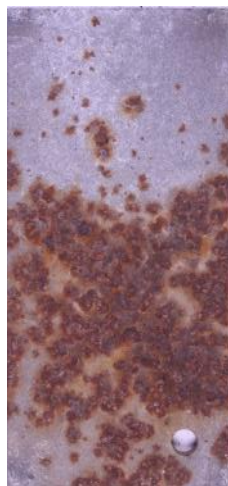
Groundward

Skyward

Groundward



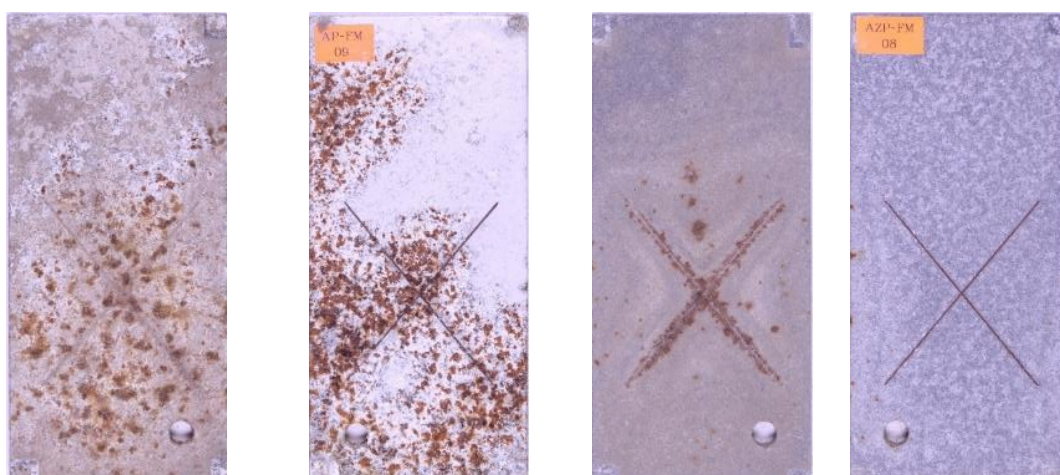
(a) University of the Ryukyus



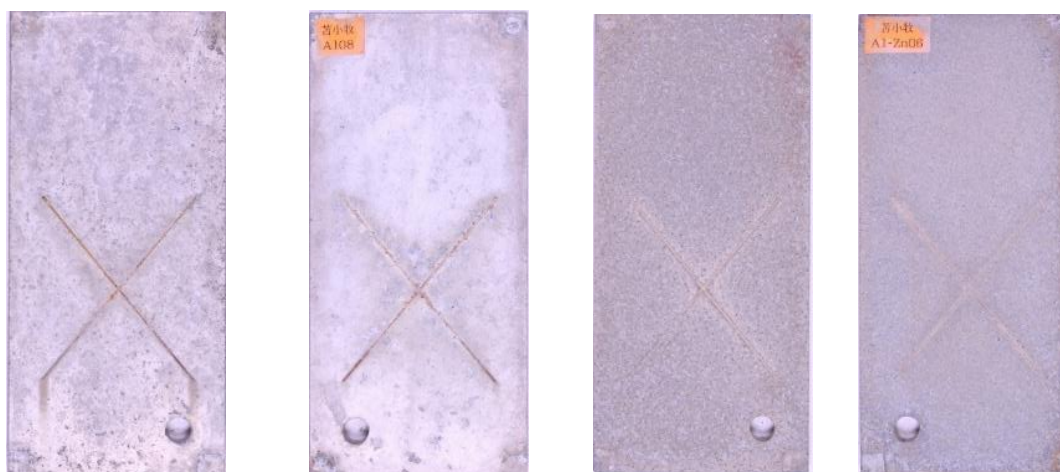
(b) Kyoda



(c) Kyushu University



(d) Momochi



(e) Tomakomai

Fig. 3-5 The surface condition of Al and 55Al-Zn coatings in exposure test.

The rust occurs behavior of hot-dip Al coating

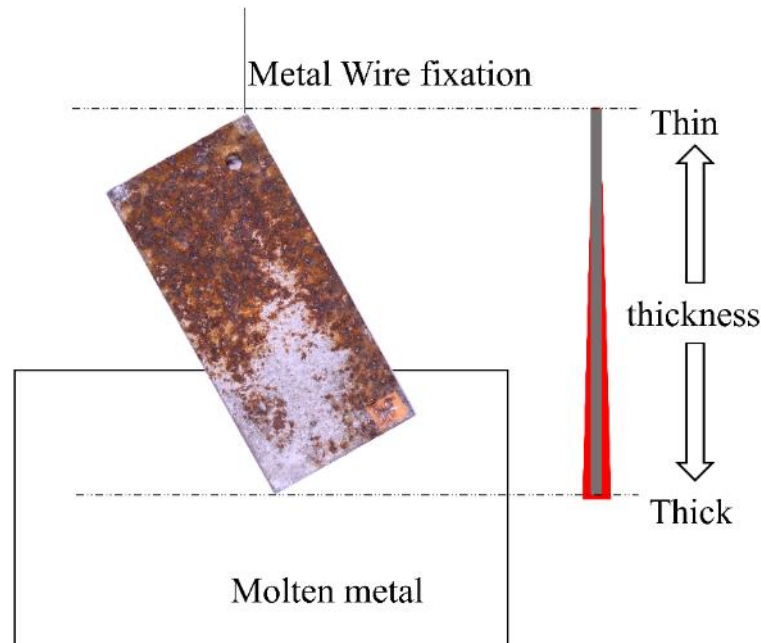


Fig. 3-6 Schematic diagram of hot-dip aluminum production process.

long as there is rain washing effect, hot-dip aluminum can still exhibit excellent shielding effectiveness. In environments with rain washing effect, hot-dip aluminum demonstrates a remarkably effective protective shielding effect. During the analysis of the appearance of the hot-dip aluminum test specimens, it was observed that, for the areas with circular holes, the surface degradation of the specimens was often smaller, and the coating was relatively intact. This is due to the uneven thickness of the surface coating during the processing of hot-dip aluminum test specimens. The production process of hot-dip aluminum test specimens involves fixing them with heat-resistant wires and other weight-bearing devices reserved on the steel structure. The specimens are then slowly immersed into the molten metal solution, raised slowly after a certain period, and finally become finished products after the cooling and drying process. The schematic diagram of the production process is shown in Fig. 3-6. Due to the fluidity of the plating solution, there is inevitably a problem of thinner coating at the upper part and thicker coating at the lower part during the lifting process. Generally, thicker coatings often have better corrosion resistance because the lower part, i.e., the area away from the circular holes, tends to experience less severe degradation during the lifting process [132].



Skyward

Groundward

Skyward

Groundward



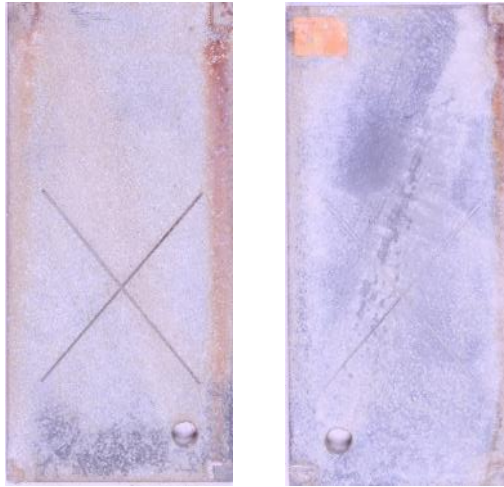
(a) University of the Ryukyus

(b) Kyoda



(c) Kyushu University

(d) Momochi



(e) Tomakomai

Fig. 3-7 The surface condition of hot-dip Zn coating after atmospheric exposure test.

To compare the hot-dip aluminum test specimens, simultaneous atmospheric exposure experiments were conducted with hot-dip Zn specimens. Hot-dip Zn, relative to hot-dip aluminum, is a more widely used metal corrosion-resistant coating. The surface condition of hot-dip Zn coating after the atmospheric exposure test is shown in Fig. 3-7. In atmospheric environments with rain washing effects (UR, KU, To), the surface corrosion of hot-dip zinc is more severe compared to hot-dip aluminum, and its color is relatively darker. Particularly in the To specimens, the surface roughness of the skyward side is more noticeable, and it loses its metallic luster. This also indicates that in atmospheric environments with rain washing effects, the shielding effect of hot-dip zinc is relatively inferior to that of hot-dip aluminum. Similarly, in atmospheric exposure areas without rain washing effects (KY, Mo), the surface deterioration of hot-dip zinc is much better than hot-dip aluminum. There is no comprehensive degradation as observed in the hot-dip aluminum specimens. This suggests that the impact of salt accumulation on hot-dip zinc is not as sensitive as on hot-dip aluminum. For locations without rain washing effects, it is recommended to use hot-dip zinc as the protective material for steel.

3.4 Evaluation of corrosion behavior after long-term atmospheric exposure test.

3.4.1 SEM-EDX surface elements analysis

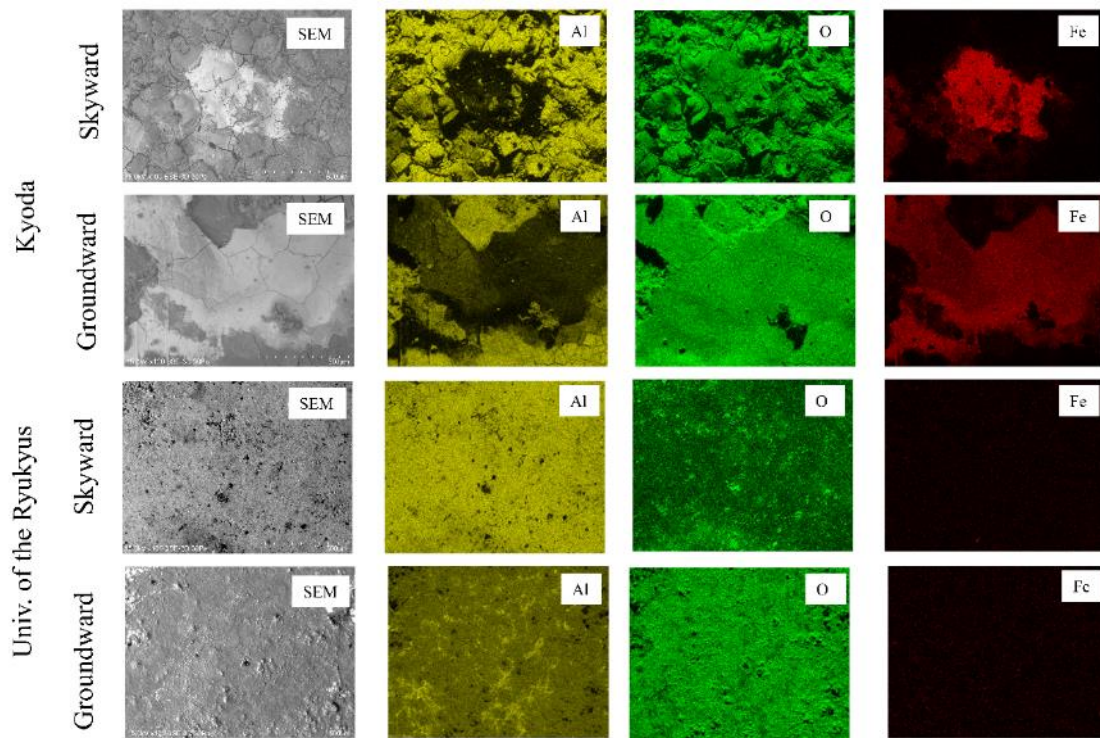


Fig. 3-8 Surface mapping of hot-dip Al coating specimen after atmospheric exposure test in KY and UR.

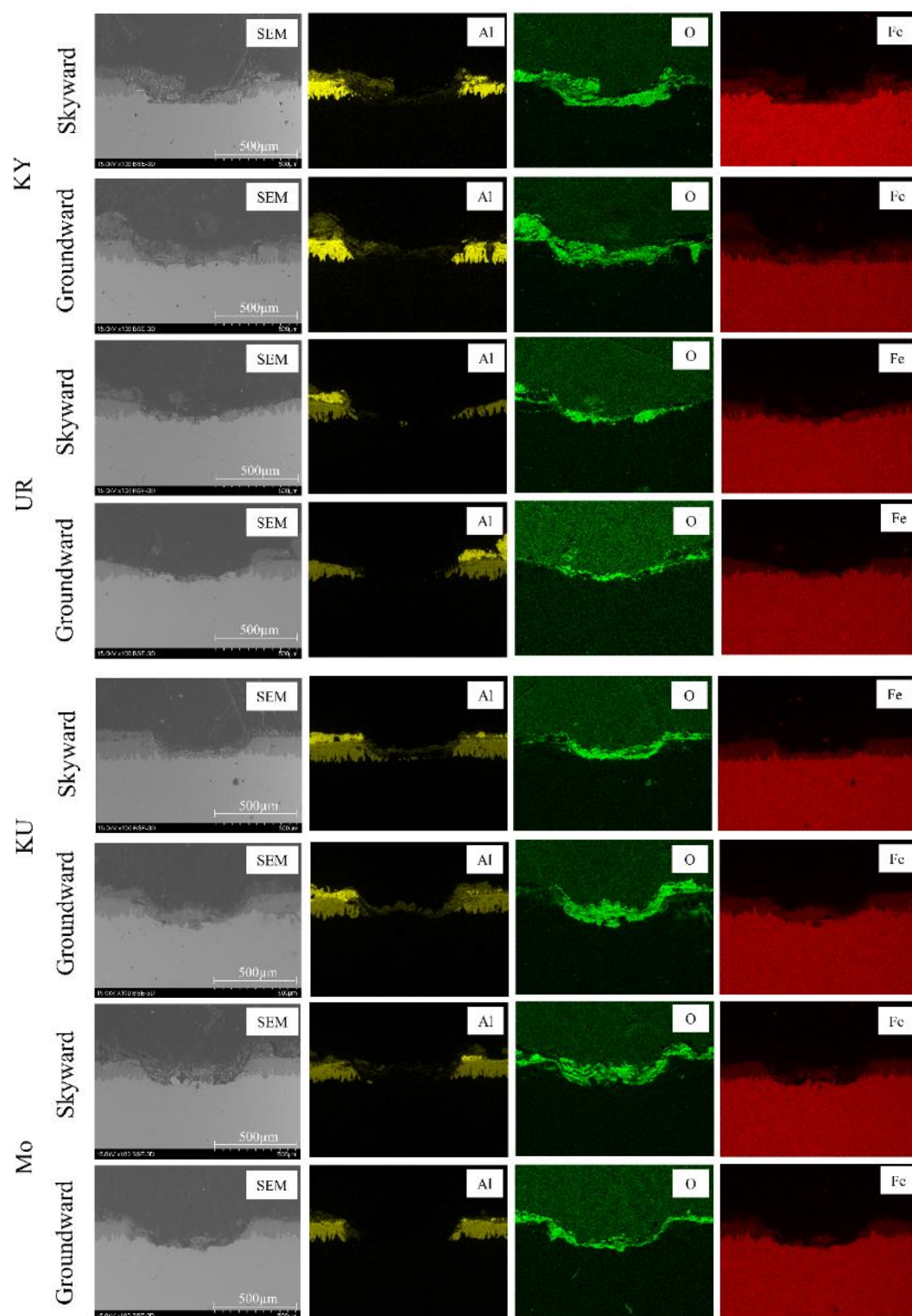
Observations from the atmospheric exposure experiment on hot-dip aluminum specimens reveal that all corrosion situations can be broadly categorized into two types: those with rain washing effects and those without this effect. The most typical examples are the KY and UR atmospheric exposure sites. Surface analyses were conducted on specimens from these two exposure sites. SEM images were captured of the KY and UR specimen surfaces, followed by elemental analysis using EDS. Yellow-brown substances appeared on both the skyward and groundward surfaces of the hot-dip aluminum exposed in KY. The SEM-EDS mapping as depicted in Fig. 3-8. The SEM-EDS analysis of KY and UR specimen surfaces. EDS surface testing of the specimens confirmed our earlier hypothesis that the yellow-brown substances were a result of iron dissolution from the

Fe-Al alloy layer after damage to the aluminum layer on the hot-dip aluminum surface. To assess the extent of corrosion progress, cross-sectional analysis of the KY specimen is required to determine whether corrosion has penetrated the Fe-Al alloy layer and affected the steel substrate.

3.4.2 SEM-EDS corrosion section elements analysis

An analysis of the cross-cut and general parts of hot-dip aluminum was conducted, and the SEM-EDS results of the cross-cut are shown in Fig. 3-9. The primary consideration in designing the cross-cut experimental specimens was to investigate the corrosion degradation of the steel substrate after direct contact with the corrosive environment. The aim was to determine whether the hot-dip aluminum coating could continue to provide corrosion protection. When the hot-dip aluminum coating is damaged, it can no longer offer a barrier to protect the steel. However, it is unclear whether it can still provide sacrificial anode protection. Through SEM-EDS mapping of the cross-cut sections, it was observed in five different atmospheric exposure sites—KY, UR, KU, Mo, and To—that even though the corrosive environment was in direct contact with the steel substrate, the mapping evaluation showed no significant leaching of iron in the embedded sections. This contrasts with previous atmospheric exposure corrosion tests on bare steel plates, where direct exposure to the atmosphere resulted in significant corrosion and the formation of a certain thickness of corrosion products. This indirectly indicates that the hot-dip aluminum coating can still offer some level of sacrificial anode protection to the steel substrate. This protective effect is consistent in both high-salinity environments without rain wash effect and environments with rain wash effect.

The cross sectional of the general part is shown in Fig. 3-10. The analysis of the cross-cut sections was conducted to investigate the protective effect of hot-dip aluminum on the steel substrate after indentations had occurred. The general corrosion condition demonstrates the protective performance of hot-dip aluminum on steel when the coating is intact. For the specimens, during the cross-sectional analysis, the entire surface of the sample was first examined, and areas with more severe corrosion were selected for focused analysis. In the cross-sectional observation of the specimens from KY, most of the cross-sections were relatively intact. However, due to the high salinity, chloride ions severely attacked the surface of the aluminum layer, leading to its deterioration. In some



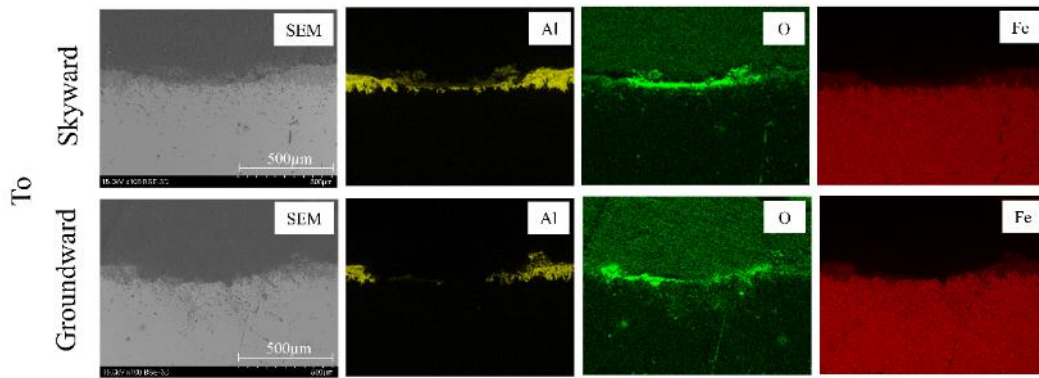
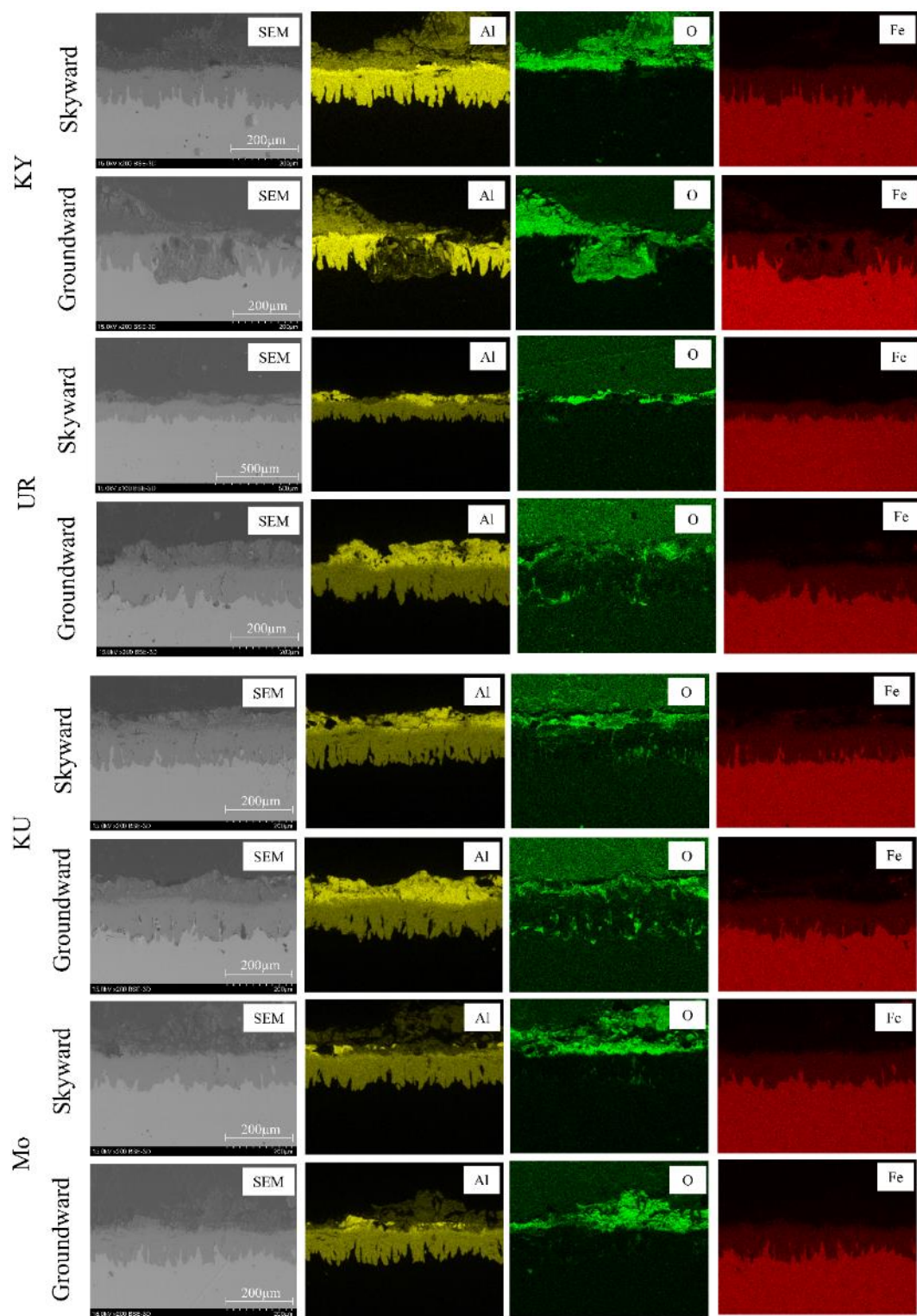


Fig. 3-9 Cross-section mapping of the cross-cut part of hot-dip Al coating specimen after atmospheric exposure test.

areas, the corrosion extended from the surface aluminum layer to the steel substrate, progressing to the aluminum-iron alloy layer. Similar issues were observed in the specimens from Mo, where the surface aluminum had deteriorated significantly, and corrosion continued to spread.

However, in the atmospheric exposure sites with rain wash, such as UR, KU, and To, the surface aluminum layer remained relatively intact. Observations of the specimens' exterior showed that, even after eight years, there was virtually no corrosion. For the atmospheric exposure experiment of hot-dip aluminum in KY, it was observed that the outermost aluminum layer of the hot-dip aluminum was almost completely absent in both skyward and groundward directions. Corrosion had progressed to the alloy layer, and though yellow-brown corrosion by-products appeared, the alloy layer remained clearly visible. Corrosion was confined to the Fe-Al alloy layer and did not extend further downward. Previous studies on a quay used in a marine environment for 25 years indicated that, despite long-term corrosion in a high-salinity environment, the skyward side showed almost no signs of corrosion due to rain washing effect. The quay, constructed with a truss structure, experienced a high airborne salt environment without rain washing on the ground side due to the shielding effect of the steel structure. Even in such an extreme and prolonged corrosion environment, the Fe-Al alloy layer remained sound after extensive corrosion. This suggests that the alloy layer maintains excellent corrosion resistance in corrosive environments. In the UR exposure site with rain washing effect, the general parts of both skyward and groundward sections were in excellent condition, exhibiting no visible signs of corrosion. The outermost aluminum layer remained intact, providing long-term protection to the steel structure in this environment.



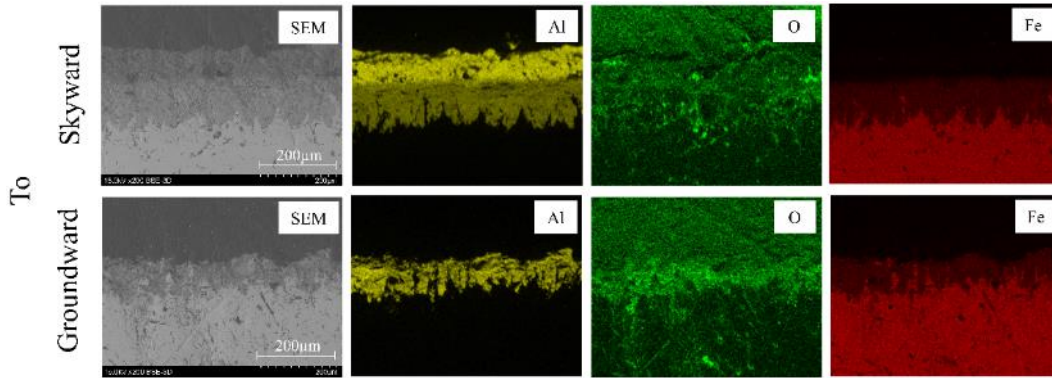


Fig. 3-10 Cross-section mapping of general part of hot-dip Al coating specimen after atmospheric exposure test.

3.5 Consideration of hot-dip Al coating in the atmospheric environment.

3.5.1 Overview of the corrosion of Al in the atmospheric environment

Al is one of the most widely used metals, competing with steel and increasingly applied in construction (for wall panels and window decorations), transportation, and public engineering, where the corrosive medium is the atmosphere. Therefore, Al is often exposed to both indoor and outdoor atmospheric conditions. The affinity of Al to oxygen allows it to form an oxide film at room temperature, exhibiting excellent characteristics in adhesion, continuity, and corrosion resistance. When Al comes into contact with air, direct oxidation spontaneously forms a thin, dense, tough, and inert (passive) natural oxide film (aluminum oxide, Al_2O_3), providing significant protection to the Al substrate. Depending on the conditions of its formation, the thickness of the aluminum oxide film can vary between 40 to 100 nanometers. In the long-term atmospheric corrosion, the corrosion rate of the Al can be described at the general equation [100,133].

$$R = At^n \quad (7)$$

The R and A can be calculated by the exposure time t and the mass losses after the exposure test.

This Al oxide film consists of two layers: a denser layer closest to the aluminum base (barrier layer) with a thickness of 20-25 nanometers, and an outer layer of more permeable thin aluminum hydroxide ($\gamma\text{-AlOOH}$) or bayerite [$\text{Al}(\text{OH})_3$], the thickness of which slowly increases with the increase in atmospheric humidity. Some studies focus on the characterization of Al oxide. This natural Al oxide film is stable in environments with

close to neutral pH values but dissolves in acidic or alkaline media. Atmospheric corrosion of aluminum primarily manifests in two forms: loss of luster, manifested as a widespread loss of shine or isolated stains related to the condensation of moisture (also known as staining); and pitting. The former cannot accurately be termed an attack and precedes the formation of pits. Pitting occurs in the defective areas of the natural oxide film, such as low-thickness or fractured areas of the natural oxide film, vacancies, areas with dislocations, impurities, alloy elements, etc. Once exposed to the atmosphere, the aluminum surface degrades, forming various corrosion products.

A three-layer structure has been identified: aluminum itself and its natural oxide; a corrosion layer on the aluminum oxide; and a surface contamination layer. Sulfate substances are the most abundant components in the corrosion layer, although chloride substances are also common. In the natural environment, typical corrosion reactions involve the formation of aluminum hydroxide by combining with water (constituting corrosion products and covering pits in the form of voluminous mounds) and the generation of hydrogen [75,134]:



The accumulation of hydrogen gas in the outermost layer of the base Al leads to the formation of blisters on the metal surface, consistent with the presence of nodules on the base aluminum. Unlike the widespread material thickness loss resulting from corrosion of other metals, aluminum corrosion is often localized, forming numerous cavities (pits) across the entire surface, keeping large metal areas intact between them. In this scenario, the concept of average penetration becomes meaningless, and it is more accurate to express corrosion as a mass loss per unit surface area [135]. The formation of pits on the surface is the most common corrosion type for aluminum alloys exposed to the atmosphere, especially in marine atmospheres. In certain highly corrosive industrial environments, there is documentation indicating the possibility of extensive corrosion.

When Al and its alloys exposed to the atmosphere, especially in marine atmospheres, the formation of pits on the surface is the most common type of corrosion. In certain highly corrosive industrial environments, widespread corrosion is possible. The resistance of aluminum to pit formation depends on its purity, with the purest materials generally being the most corrosion-resistant. Therefore, high-purity aluminum typically

exhibits fewer pits, although these pits may be deeper than those in less pure aluminum or alloys. The presence of other elements, whether impurities or intentionally added alloying elements, increases the material's sensitivity to pit formation. Like other metals, atmospheric corrosion of aluminum is strongly influenced by the presence of moisture [89,136,137]. A key consequence of having a layer of water on the metal surface is that it provides a medium for the mobilization of aluminum cations and the deposition of anions. All studies unanimously agree that aluminum rapidly forms a thin film of aluminum oxide upon initial contact. In continuous exposure, this film may grow and transform into various other atmospheric products. Aluminum oxide (Al_2O_3) is the first component formed after exposure to the atmosphere, with an initial depth of 2-3 nanometers. After several months in the air, this oxide is covered by a thin film of boehmite ($\gamma\text{-AlOOH}$), subsequently followed by bayerite ($\text{Al}(\text{OH})_3$), also written as $[\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}]$ [27,138].

The structure of the oxide film formed on aluminum exposed to the atmosphere has been extensively examined using electron microscopy. In the presence of water or water vapor, the outer skin of the oxide film on aluminum can transform into a hydrated form. The resulting film is typically highly porous, and it is evident that part of the hydration process represents a chemical conversion into hydroxide minerals.

3.5.2 The effect of the environmental factors

Compared to many other metals, aluminum corrodes relatively slowly when exposed to the atmosphere. The corrosion of aluminum, expressed as mass loss per unit surface area, progresses linearly with wet time, at least during the initial 2000 hours (the longest study period). When aluminum is exposed to pure air, the influence of relative humidity ($RH\%$) is generally negligible [8]. In fact, the corrosion of aluminum and its alloys primarily depends on atmospheric pollution, typically by sulfur dioxide or chloride, and wet time only plays a decisive role in the corrosion process under such contamination conditions. The indoor corrosion rate of aluminum is affected by $RH\%$, as corrosion begins only at around $RH70\%$. At this point or above, aluminum corrosion products absorb sufficient moisture to stimulate the chemical degradation process.

Little is known about the impact of temperature on atmospheric corrosion of aluminum. The corrosion rate of aluminum covered by a liquid film almost doubles

between 1 and 5°C, but remains relatively constant above this temperature until 15°C (the highest studied value). Therefore, variations in temperature seem to have little effect on the corrosion of aluminum and its alloys over a wide temperature range when the surface is moistened by precipitation (rain, mist, dew). In laboratory experiments, it is known that SO₂ enhances the corrosion of aluminum. After several days to weeks, stable, highly insoluble aluminum sulfate of an alkaline nature is formed through a series of reactions can be described as follow [137,139,140]:



The amount of SO₂ absorbed on the surface of aluminum significantly increases with increasing humidity, leading to the formation of sulfuric acid [8,132,141]. Sulfuric acid can disrupt the naturally occurring oxide film that spontaneously covers the metal surface, thereby accelerating corrosion [142,143]. Amorphous hydrated aluminum sulfate has been observed as the most abundant corrosion product of aluminum exposed to marine and industrial atmospheres. Analysis of existing data indicates that the corrosion rate of aluminum in industrial atmospheres is significantly accelerated. The corrosion rate of aluminum in industrial atmospheres is seven times higher than in rural environments. Chloride ions are a significant contributor to the degradation of aluminum surfaces under atmospheric exposure [57,144,145]. Chloride ions often perforate and damage the protective oxide film on aluminum. Therefore, atmospheric chlorides constitute a specific medium for aluminum corrosion, with chloride concentrations in marine atmospheres being 22 times higher than those in rural atmospheres, as reported in their experiments. In other studies, experiments suggest that aluminum mass loss due to corrosion is six times higher in atmospheres contaminated with chlorides. Chlorides enter the surface layer of water through the introduction of gaseous HCl or organic gases containing chlorides or through the deposition of sea salt, background aerosol particles, or precipitation. Once present, chemical reactions can produce aluminum chloride or hydroxychloride, whose solubility means they are mostly washed out of the corrosion product layer by rain. Surprisingly, there is little fundamental and empirical research focused on revealing the possible quantitative relationship between aluminum corrosion (mass loss) and the concentration of SO₂ in the atmosphere.

3.5.3 Corrosion characteristics of pitting corrosion

Aluminum forms a relatively stable oxide film, protecting it from the effects of mildly corrosive atmospheres. However, in atmospheres containing corrosive salts and gases, this film loses stability, and the material begins to undergo attack, usually resulting in pitting. Pitting corrosion may occur even before the mass loss reaches a significant level. Therefore, when designing aluminum structures, it is advisable to consider the predictable penetrability of pits that may form on the metal. In the initial years of atmospheric exposure, the growth rate of the maximum pit depth is relatively high but gradually decreases to a near-constant value over time [146–148]. The maximum pit depth (h) is estimated to be related to the exposure time (t) by the following formula:

$$h = K \cdot \sqrt{t} \quad (10)$$

The stability of pit depth over time is attributed to the presence of aluminum oxide, which covers the pits and acts as a certain barrier [148]. Long-term experiments conducted in different regions and tests in various atmospheres indicate that the pit depth of aluminum essentially ceases to evolve after the second year of exposure. Long-term atmospheric exposure tests show that mass loss increases almost linearly, while the penetration rate of deep pits rapidly decreases over time. However, these two facts are not necessarily contradictory, as pits also grow in diameter beneath the aluminum surface and progress in a manner similar to the way termites attack wood, forming tunnels. The corrosion characteristics of common forms occurs in pitting corrosion development is shown in Fig. 3-11.

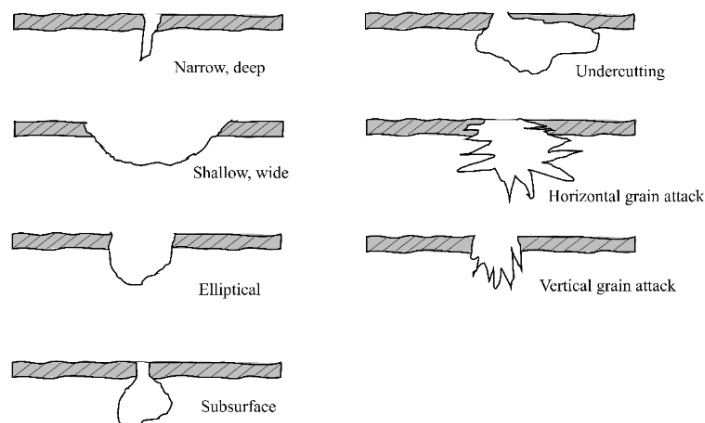


Fig. 3-11 Common forms of pitting corrosion development.

It is generally not possible to determine any differences in pit penetration between the sample surfaces facing the sky and facing the ground, and when such differences exist, they usually do not exceed 20-30%. The deepest pits are always found on surfaces facing the ground. Surfaces facing the sky often bubble up more rapidly than surfaces facing the ground, especially in industrial environments. This behavior may be attributed to the influence of corrosive particles deposited on the surface facing the sky. The maximum pit penetration (h) as a function of time can be fitted using a semi-logarithmic expression [149].

$$h = a \log t + b \quad (11)$$

where a is a constant, b is the maximum pit penetration in the first year, and t is the exposure time in years. Both a and b depend on the alloy type and atmospheric corrosiveness. Due to the logarithmic nature of the relationship, the attack significantly diminishes over time, which is not practically severe. After 20 years of exposure in marine atmosphere, the pit depth remains less than 1 millimeter. Establishing a connection between pitting depth (h) and mass loss (m) can be interesting, especially considering the ease of obtaining gravity data [100,150]. A semi-logarithmic relationship between the maximum pit depth ($h_{\max}$) and mass loss (m) is proposed:

$$h_{\max} = h \log m + k \quad (12)$$

Where h and k are constants.

This study investigates the long-term corrosion of aluminum exposed to various atmospheres. In rural and urban atmospheres, aluminum corrosion is very low, with no observed deep pits but isolated shallow pitting in the form of tiny hemispherical attacks on rain-protected surfaces, leading to the formation of a crack layer. In industrial and marine atmospheres, aluminum exhibits noticeable degradation, and numerous corrosion pits with a depth of approximately 100 μm are observed [151]. The presence of sulfur and chloride compounds is noted in the corrosion products, especially following the rupture of a thicker (60-70 μm) bayerite layer. It is noteworthy that chloride compounds occupy preferential positions within the corrosion pits [152].

3.6 Summary

In this chapter, long-term atmospheric exposure test of the hot-dip aluminum coating carried on five atmospheric exposure sites were mostly located not far from cities and coastline. At the same time, hot-dip 55Al-Zn and Zn coatings were also studied for a comparison with aluminum coating. The surface observation and cross-section analysis were studied, the following conclusions were drawn below.

- (1) Through long-term atmospheric exposure experiments, it was found that for hot-dip aluminum, the presence or absence of rain wash effect significantly affects its durability. Hot-dip aluminum is sensitive to environments with high airborne salt accumulation. The outmost aluminum layer is prone to pitting corrosion in salt-rich environments, leading to overall degradation of the aluminum layer.
- (2) In environments with rain wash effect, even under conditions of high airborne salt, hot-dip aluminum exhibits excellent protective performance.
- (3) Comparing hot-dip aluminum, 55Al-Zn, and Zn coatings, hot-dip aluminum demonstrates superior shielding performance in environments with rain wash effect. In environments without rain wash effect, the aluminum layer degrades earlier than the other two metal coating layers.
- (4) Even if the surface layer of hot-dip aluminum deteriorates, the Fe-Al alloy layer still possesses excellent protective capabilities to prevent corrosion of the steel substrate in corrosive environments.

CHAPTER 4 GALVANIC CORROSION BEHAVIOR OF HOT-DIP ALUMINUM AND METAL COATINGS APPLIED TO STEEL BOLTED JOINTS

4.1 Introduction

Corrosion damage is a mainly factor in reducing the durability of steel structures [13,57,58]. Zn coatings have been widely applied for protection of steel structures in various atmospheric environments [59]. After a hot-dip Zn coating process, the corrosion resistance of steel structures is improved by approximately 20-25 times compared to that of a bare steel structure [17,60]. Zn coating is an effective and economical method of corrosion protection. It can also provide cathodic protection to steel when the coating layer is defective [25]. However, because of the sacrificial anode effect, Zn is easily dissolved in the natural environment, and the high levels of Zn will disturb the ecosystems in natural water. Further, the price of Zn is not stable, particularly for industrial applications. Moreover, the Zn coating has low anti-corrosion performance in industrial environments. Therefore, Al-based coatings are attracting increasing attention [36]. Aluminum coatings can be used in environments with both anti-corrosion and high-temperature requirements, for example, in motor vehicle exhausts and domestic appliances (e.g., cookers, dryers, and heating boilers). This is due to the formation of the fine and dense Al_2O_3 on the surface of outermost coating, which has a better oxidation resistance in the actual application [23,43]. The Aluminum coating has better anti-corrosion ability and does not easily dissolve in the environment. Aluminum and Al-based coatings are used as alternatives to Zn coatings in automobiles and construction materials as they have less weight and achieve higher performance in terms of high temperature oxidation resistance [47]. The Aluminum coating consists of an outer Aluminum layer whose chemical composition is close to that of the hot-dip bath. The intermetallic layer consists of FeAl_3 and Fe_2Al_5 phases [37]. The main disadvantage of the intermetallic layer is its brittleness, and cracking and peeling off may occur during use. To reduce this detrimental effect, Si is added to the Aluminum dipping bath in amounts of 1-10 wt%. Si

reduces the growth of intermetallic layers, particularly the Fe_2Al_5 layer [38]. Panossian et al. researched the cathodic protection effect of Aluminum and some kinds of Al-based coatings in the atmospheric environment. The Aluminum coating can provide the cathodic protection to the steel substrate in a high concentration of chloride present environment [17,60]. Lemmens et al. studies the electrochemical properties of hot-dip Al coating in the chloride environment and indicated that the outermost Aluminum coating layer can be dissolved and had a sacrificial protection effect to the underlying layer (including the intermetallic layer and steel substrate) [61]. These results also indicate that the Aluminum coating has a better shielding effect and a certain sacrificial anodic protection for steel in a chloride environment. In addition to Zn and Al coatings, new-generation Al-alloy coatings have been investigated. Among the Al-based coatings, three types have been widely applied for steel structure protection, namely, 55Al-Zn and Zn-5Al, which are used in the continuous hot-dip coating industry, and Zn-15Al, which has many applications in thermal spraying [60]. The most commonly used Al-based alloy coating is the 55Al-Zn coating, also called galvalume. The chemical composition of the 55Al-Zn coating is approximately 1.6% Si, 43.4% Zn, and 55% Al (weight percent) [24,25]. In the microstructure, this type of coating also consists of two clear and distinguishable layers: an outer Al-Zn layer and a very thin intermetallic layer [3]. Compared to the Aluminum coating, the thicknesses of both the 55Al-Zn coating layer and the intermetallic layer are significantly reduced. Based on this characteristic, the 55Al-Zn coating is used for some small steel members (e.g., bolts, nuts, and washers). The bolt and nut should fit well to provide the required mechanical properties and a simple assembly. The 55Al-Zn coating can meet the requirements for small steel members. For large steel structures, continuous hot-dip Al coating remains the most economical method for mass production [62]. The bath temperatures of the three coatings are 440–460 °C (Zn), 595–610 °C (55Al-Zn), and 700–750 °C (Al) [23,63,64]. The heat input to the microstructure formed in the heat-affected zone is effective and affects the mechanical properties of steel structures [65]. Hence, the hot-dip Al coating has a significant heat effect on the steel members during the dipping process compared to the other coatings. The heat effect on small steel members is more severe than that on large steel structures. Furthermore, tiny steel members are usually coated with 55Al-Zn or Zn because of the smaller heat effect and

thickness. The different types of coatings used in bridges are shown in Fig. 4-1 (inspection device for the maintenance of bridge substructures). The steel plates were coated with Al, whereas the bolts, nuts, and washers were coated with 55Al–Zn or Zn. If the metal materials are exposed to atmospheric or aqueous environments without a protective coating, the surface of the metal will be continuously oxidized, and electrochemical reactions will continuously occur at the interface between the surface and the environment. Galvanic corrosion often occurs when two different metals are contacted in a water accumulation environment, whereas noble metals are usually protected [66]. In this study, the galvanic corrosion behavior of different metals, corrosion current density, and effect of the area ratio between the anode and cathode were evaluated by means of electrochemical tests. The atmospheric exposure test described the galvanic corrosion behavior in actual situations and practical applications. The corrosion products of the specimens after the atmospheric exposure and electrochemical tests were analyzed using XRD.



Fig. 4-1 Inspection device for maintain management of bridge substructure.

4.2 Experimental

4.2.1 Specimens

The specimen in the exposure test included two components: a common low-carbon steel plate coated with hot-dip Al coating and M16 bolt with hot-dip 55Al–Zn (Composition by the wight percent: 55 % Al, 43.4 % Zn, 1.6 % Si) coating. The steel plates (length: 150 mm, width: 70 mm, thickness: 6 mm) were fabricated based on JIS G 3106 SM490A and fixed by M16 bolts at the central position. The coating types and exposure sites were listed in Table 4-1. For the electrochemical tests, the sizes of the specimens were 100 mm (length) $\times$ 50 mm (width) $\times$ 5 mm (thickness). The steel substrate was also SM490A and coated with Al and 55Al–Zn coatings. The thicknesses of the Al and 55Al–Zn coatings were 80 and 67 μm , respectively. The hot-dip coating process was provided by the shinko alumer industries company. The thickness was measured by the electromagnetic film thickness meter SM-1000 (Sanko Electronic Laboratory Co. Ltd.).

Table 4-1 Specimens exposed in the University of the Ryukyus (UR) and Kyoda (KY).

Exposure site	Coating materials		Mark on the specimens
	Bolt and washer	Steel plate	
University of the Ryukyus	55Al–Zn	Al	UR
Kyoda			KY

4.2.2 Electrochemical test

Electrochemical tests were performed at 20 ± 2 °C with the electrolyte at rest. The specimens were exposed to 0.1 and 3.5 wt% NaCl aqueous solutions and exposure to the laboratory atmosphere without stirring. The 0.1 and 3.5 wt% NaCl solutions simulated the salt content of rainy and seawater, respectively. Open circuit potential (OCP) measurements were performed using a potentiostat (Princeton Applied Research). The OCPs were measured with respect to the reference electrode, in which Ag/AgCl was immersed in saturated potassium chloride. The OCPs of the specimens in NaCl solutions of different concentrations were continuously monitored for 48 h, and the measurement

interval was 5 s. After the test, the theoretical galvanic current density was calculated from the potential difference and the sum of the resistance of the anode, cathode, and solution [66]. The resistance of the electrochemical test system was measured using impedance spectroscopy and a metal resistance measurement system [67,68]. In the galvanic current test, two concentrations (0.1% and 3.5%) of neutral NaCl solution were employed. The electrolyte used during the electrochemical tests was used without external stirring. The configuration and connection methods of the galvanic-current test are shown in Fig. 4-2. The specimens were covered with polytetrafluoroethylene to isolate the solution and to control the contact area of the galvanic corrosion reaction. In general, for the exposed bolt specimen, the area of the Al-coated steel plate should be considerably larger than those of the 55Al–Zn-coated bolt and washer components. Therefore, to simulate the actual situation and verify the changing area ratios of the cathode to the anode, the galvanic currents were measured by changing the area ratios in the electrochemical test. A pair of specimens coated with 55Al–Zn and Al coatings were connected using a zero-resistance ammeter SACM–30F (Syrinx Inc). A wire was used to contact the electrodes and the zero-resistance ammeter. The per unit length resistance of the wire was $6.29 \times 10^{-2} \Omega/\text{m}$. (Fuji Electric Wire Co., Ltd.). A group of specimens were placed in parallel and kept at a distance of 2 cm. By changing the immersed areas of the Al coating (S_{Al}) and 55Al–Zn coating ($S_{55\text{Al-Zn}}$), the area ratios ($S_{\text{Al}}/S_{55\text{Al-Zn}}$) were set to 1, 2, 3, and 4. In the electrochemical test, the area of 55Al–Zn was constant (8 cm^2). However, the area of the Al coating always changed. To control the variables, the current density was calculated as (total galvanic current μA)/(area of 55Al–Zn coating 8 cm^2).

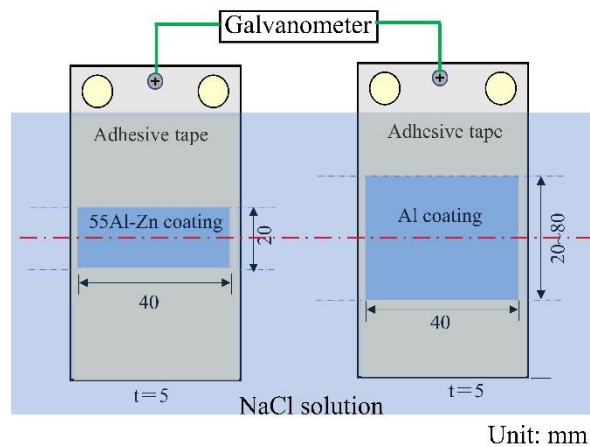


Fig. 4-2 Configuration of the galvanic current test.

4.2.3 Atmospheric exposure test

Atmospheric exposure tests were carried out at the two sites (Kyoda, Univ. of the Ryukyus) in Okinawa. The exposure period was from October 2017 to September 2021, approximately four years. After the exposure tests, the specimens were returned for analysis. The exposure locations were 1) University of the Ryukyus (Longitude: $127^{\circ} 46'$ E, Latitude: $26^{\circ} 15'$ N denoted as UR), with rain-washing effect outdoors, 2) Kyoda (longitude: $127^{\circ} 57'$ E, latitude: $26^{\circ} 32'$ N denoted as KY) located under the viaduct of the highway at the distance of approximately 30 m from the west coastline, without rain-washing effect. The locations of the exposure sites are shown in Fig. 4-3. The surface appearance during the exposure test is shown in Fig. 4-4. All the specimens were placed in an angle steel frame, and the rain-washing effects on the skyward and groundward portions of each specimen were compared. Environmental data for the exposure sites are presented in Table 4-2.



Fig. 4-3 Location of the exposure sites.

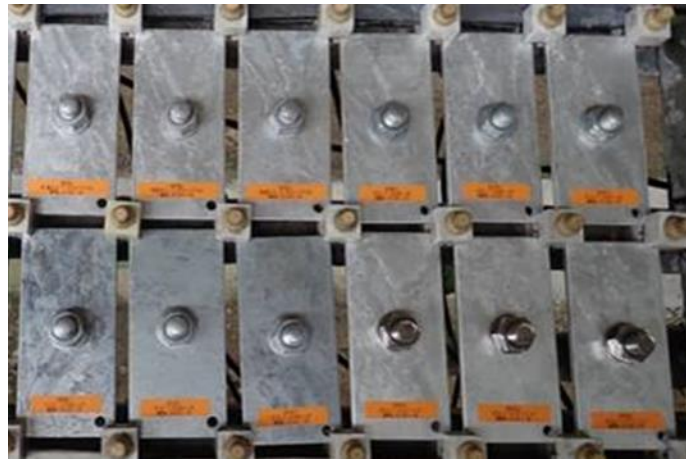


Fig. 4-4 Surface appearance of exposed specimens.

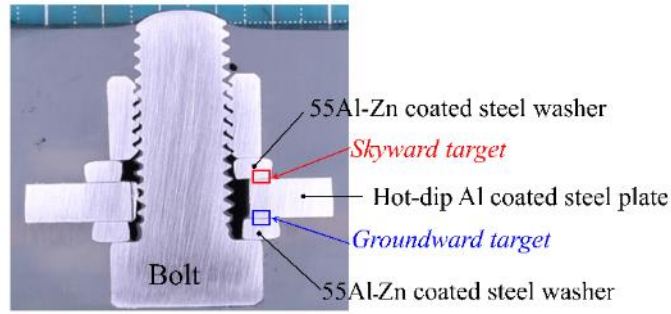


Fig. 4-5 Sample of exposure test after cutting and polishing.

Table 4-2 Environmental data of the two exposure sites measured by EL-USB-2 sensor (Lascar Electronics Inc.) (2017–2021)

Exposure site	Temperature T (°C)	Humidity RH (%)	Airborne salt w (mdd)	Offshore distance (m)	Average precipitation on (mm/day)	Rain washing effect
UR	22.9	81.5	0.30	2300	5.20	Yes
KY	22.7	82.9	0.50	30	5.30	No

4.2.4 Surface condition and cross-sectional analyses

After four years of exposure testing, the exposed specimens were fixed using an epoxy resin. Epoxy resin was used for fixation during cutting to ensure the integrity of the bolt and steel plate. Subsequently, the specimens were cut along the vertical central line at approximately 2 mm, and the cross-sectional surface was polished near the central line for cross-sectional observation and element analysis. In both the cutting and polishing processes without water, the sandpaper range was from #400 to #2000. A sample of the specimen after machining and polishing is shown in Fig. 4-5. The cross-sections microstructures of the atmospheric exposure specimens were obtained using a scanning electron microscope (SU3500, HITACHI Inc.). The element distribution was analyzed using energy dispersive X-ray spectrometry (EDS). The specimen was disassembled into small parts after cross-section observation to obtain more corrosion products on the surface of the bolt-jointed parts after the exposure test. The corrosion products of electrochemical test were collected from the surface of the specimens. The crystalline phase compositions of the corrosion products were analyzed using XRD (SmartLab,

Rigaku Inc.). The scanning speed of the XRD spectrum was 2°/min, and the scanning angle ranged from 10° to 80°.

4.3 Electrochemical test results of hot-dip aluminum coating

4.3.1 Potential-time and galvanic current measurements of specimens

The total current and current density can be used for evaluating the intensity of the galvanic corrosion. The changes in the galvanic currents for the Al and 55Al-Zn circuits with time at different area ratios are shown in Fig. 4-6. The area of the 55Al-Zn coating was an 8 cm² rectangle (length: 4 cm, height: 2 cm). The area of the Al coating was changed to 8, 16, 24, and 32 cm² (by controlling the length of the width direction and changing the length of the height direction). That is, the area ratios of the Al and 55Al-Zn coatings were 1, 2, 3, and 4. At the early stage of galvanic corrosion, the galvanic current increased steadily for 6 h. Subsequently, the current fluctuated within a certain range, and finally, the galvanic current continuously decreased. Changes in the area ratios of the cathode and anode resulted in a similar tendency. Galvanic current shows different absolute values on the effect of changes in diverse area ratios. In the early stage, the increasing of galvanic current may be caused by the roughening of electrode surface as the corrosion progress. The fluctuation of the galvanic current was related to the

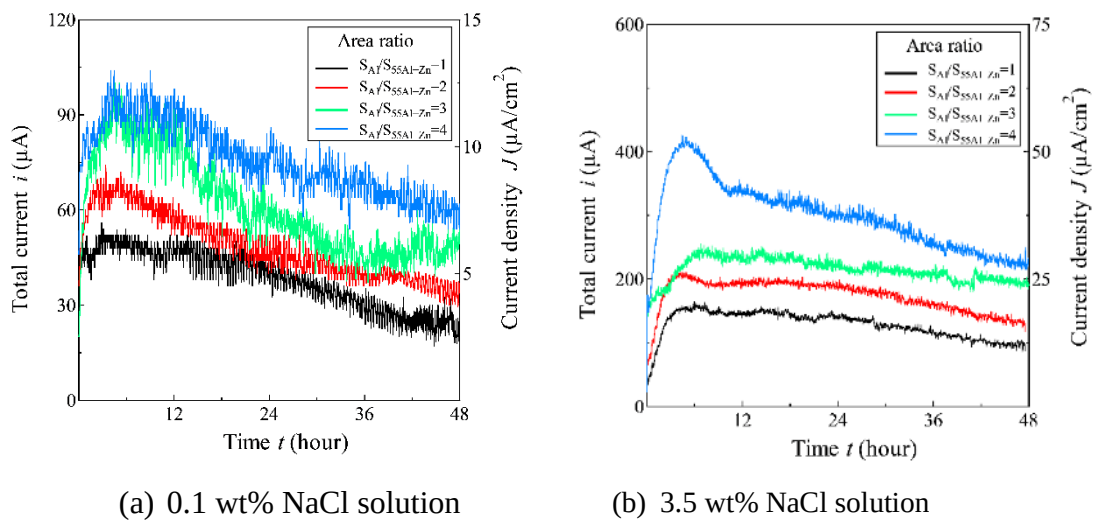


Fig. 4-6. Change in total galvanic currents for the Al and 55Al-Zn circuits with time at different area ratios.

competition between beginning and cessation of corrosion on some area. It is also described that the corrosion will stop on the corroded area and beginning in the other new area [66]. An obvious trend can be observed when comparing the current density in the 0.1 wt% and 3.5 wt% NaCl solutions: the current density at a higher concentration is much higher than that at a low concentration. The galvanic corrosion continued, and corrosion products accumulated in the anode. During the electrochemical test in NaCl solutions, simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$) and zinc aluminum carbonate hydroxide were obtained from the corrosion products. Simonkolleite is a dense and adherent material that can exhibit a certain barrier effect [69,70]. The thick corrosion product layer blocks the diffusion of ions and effectively stops the invasion of the corrosive medium [71,72], suggesting that the galvanic current of the electrochemical corrosion process can be reduced. Therefore, the galvanic current continuously decreased over the peak. The cathode of the circuit was Al because it had a nobler potential than that of the 55Al–Zn alloy metal. 55Al–Zn acted as the anode and continuously provided a sacrificial anode protection. The OCP measurements of the two different metal coatings at different concentrations of the NaCl solution are shown in Fig. 4-7. In the 0.1 wt% NaCl solution, $E_{\text{Al}} - E_{55\text{Al-Zn}}$ is approximately 0.256 V. The solution resistance of the circuit can be approximated as a constant during the test. The potential difference (cathode and anode)

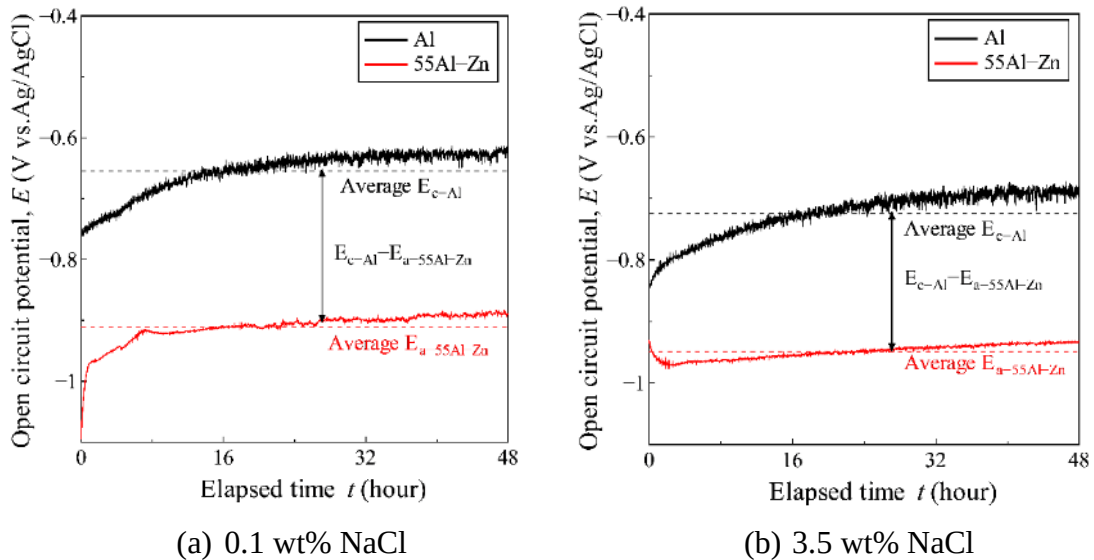


Fig. 4-7 Measurement of the OCP for Al and 55AlZn in the 0.1 wt% and 3.5 wt% NaCl solutions.

and resistance of the measurement circuit are two important parameters for evaluating galvanic corrosion. In the 3.5 wt% NaCl solution, $E_{\text{Al}}-E_{55\text{Al-Zn}}$ is approximately 0.235 V. The potential difference at 3.5 wt% concentration was smaller than that at 0.1 wt%. The galvanic current in the high concentration NaCl solution was continuously larger because the main factor of the galvanic current was the combination of different potentials and circuit resistances. The main factor is that the resistance of the NaCl solution decreases linearly with increasing concentration [73]. The average galvanic current densities of the Al and 55Al-Zn circuits at different area ratios during the electrochemical tests are shown in Fig. 4-8. In both the 0.1 wt% and 3.5 wt% NaCl solutions, for the Al and 55Al-Zn circuits, the average current increased with increasing area ratio. The relationship between the area ratio and average current density shows a good linear growth phenomenon. The slope coefficient of the relationship between galvanic current and area ratios at 3.5 wt% is 3.6 times larger than that at 0.1 wt%. This indicates that, with an increase in the Al coating area, the galvanic corrosion current also increased. In particular, at high NaCl concentrations, the galvanic corrosion behavior was more serious.

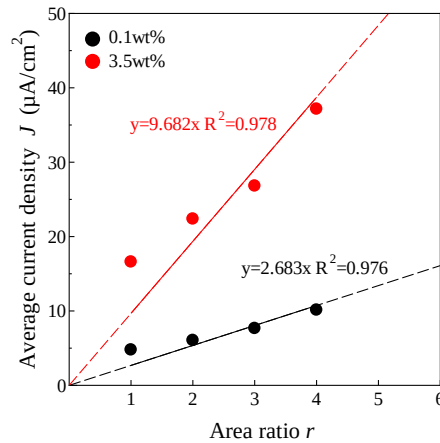


Fig. 4-8 Galvanic current density of Al and 55Al-Zn circuits in 0.1 wt% and 3.5 wt% NaCl solutions.

4.3.2 Galvanic corrosion current in the theory calculation

In the atmosphere, the rain-washing effect can also create a solution environment owing to the airborne salt dissolved in rain. In a high chloride concentration environment, galvanic corrosion also occurs because of an effective cathodic reaction. The galvanic

corrosion current is simulated by separating the components of the galvanic cells and measuring the current when they are connected externally. The corrosion rate can be described using the galvanic current [66,74,75].

$$i_g = \frac{E_c - E_a}{R_a + R_c + R_s + R_m} \quad (1)$$

where i_g is the galvanic current, R_a , R_c and R_s is the electrical resistance of anode, cathode, and solution. E_a and E_c are the potentials of anode and cathode. In this test, R_m is the resistance of the metal parts in the electrochemical measurement system, including the Al coating layer (anode), 55Al–Zn coating layer (cathode), and conductor wire between them. The resistance of the nonresistant galvanometer can be ignored. The OCP difference was measured for 48 h to obtain an average difference. The resistance R_s was obtained using a metal measuring system according to the four-point probe method. For the thick sheet sample situation, the thickness of sample (t) should be less than the distance between probes. The electrical resistance can be calculated as follows: [67,68,76]

$$\rho = \frac{\pi t}{\ln 2} \cdot \frac{V}{I} \quad (2)$$

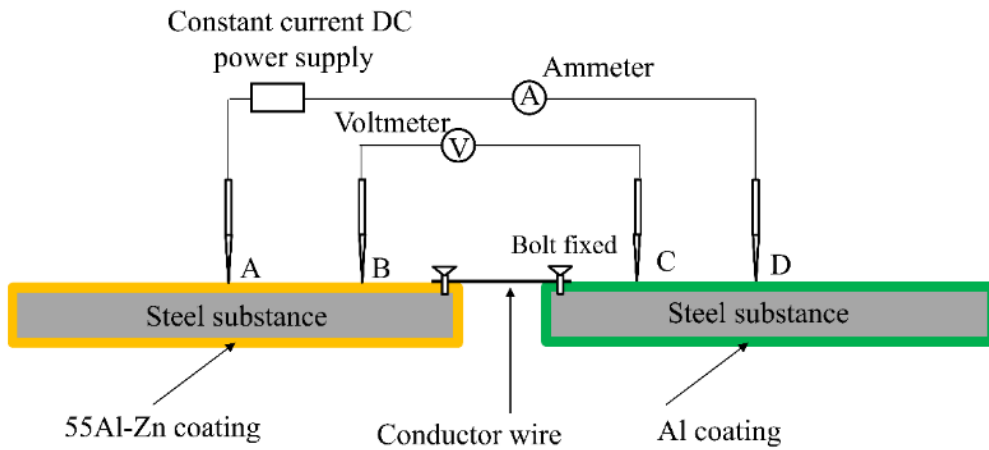


Fig. 4-9 Metal resistance measurement system.

A schematic of the metal resistance measurement system is shown in Fig. 4-9. The measurement system was an SRCM-301 electrical resistance meter according to four-probe method (Syrinc, Inc.). The resistance of the circuit system ($R_a + R_c + R_m$) was measured to be approximately 36.7 mΩ, and the resistance of this part appears like a

constant value. In addition to the metal parts, the resistance of the electrochemical system also contains a solution. The solution resistance was determined using electrochemical impedance spectroscopy [77,78]. The current-carrying ability of a solution is described in terms of conductivity, and the numerical relationship between the resistivity and conductivity is reciprocal. The principle may be expressed as follows [79]: for both metal materials and solutions, a higher conductivity indicates good electrical conductivity and poor resistance. The conductivities of the NaCl solutions at different concentrations were investigated, and the relationship between the conductivity and concentration of NaCl is shown in Fig. 4-10 [77,78]. As the concentration increased, the solution conductivity, similarly to the power function. Hunt measured the conductivity of some types of solutions and found that the conductivity of the NaCl solution has an almost linear relationship from the low to saturation concentration [80]. Lima et al. studied the electric impedances of aqueous KCl and NaCl solutions. The resistance of the NaCl solution significantly decreased with a change in the solution [73]. Comparing the galvanic current in 0.1 wt% and 3.5 wt% NaCl solutions, the potential difference of cathode and anode in 3.5 wt% is smaller than that of 0.1 wt%. The solution resistance of 3.5 wt% is also smaller than that of 0.1 wt% and has the same tendency. The galvanic current also increased because the decrease in solution resistance was considerably larger [81]. The conductivity increased with increasing NaCl concentration. Meanwhile, the solution resistance of NaCl decreased. The solution resistance was calculated from the conductivity and intervening liquid volume of NaCl solution between two electro anodes [80]. For the solution, the length was 2 cm, and the section area was 8 cm². Comparing the electrical resistivity of the electrodes and solution, the main factor that influences the galvanic current is the solution resistance, because the resistivity of the solution is many times larger than that of the metal materials. The relationship between the total resistance, that is, the sum of the solution resistance (R_s) and system resistance ($R_a + R_c + R_m$), is shown in Fig. 4-11. As the NaCl concentration increases, the total resistance decreases. In contrast, the galvanic current has an increasing tendency owing to the reduction in the resistance in the denominator of Equation (1). The total resistances at 0.1 wt% and 3.5 wt% were obtained from the fitting function above. The galvanic current densities of the 55Al–Zn and Al circuits are shown in Fig. 4-12. The galvanic current density of the test value was

measured by the electrochemical test in the situation where the reaction area of the anode and cathode was the same (8 cm^2). In a previous test, the theoretical value was calculated based on the potential difference and total resistance measured and fitted. Furthermore, a control test was carried out using Zn and Al circuits under the same conditions, and Zn and Al circuits were added for comparison.

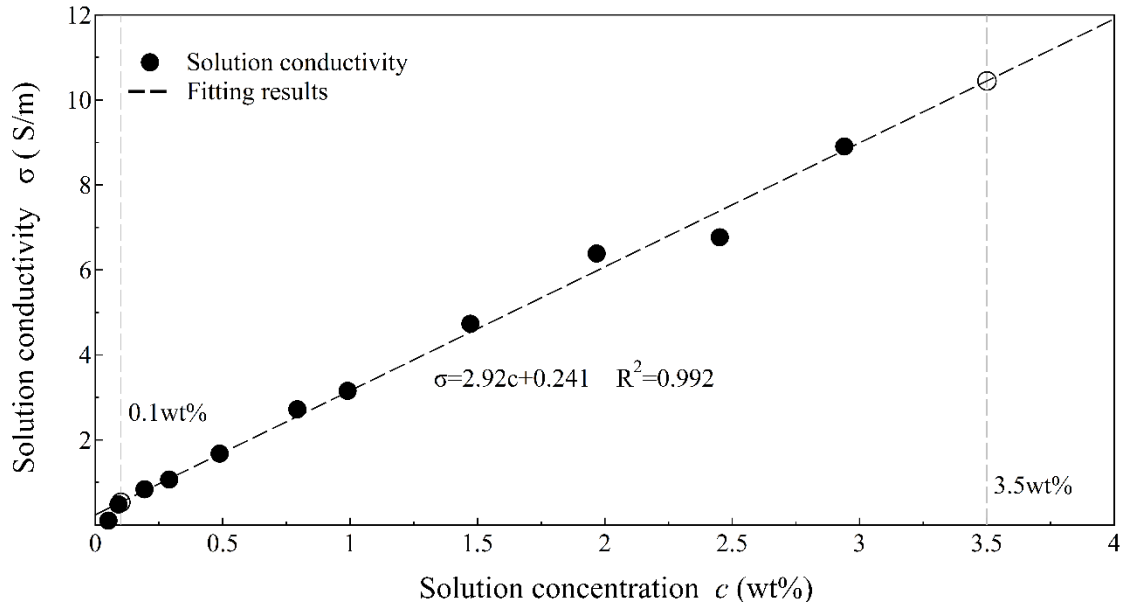


Fig. 4-10 Conductivity of NaCl solution in different concentrations.

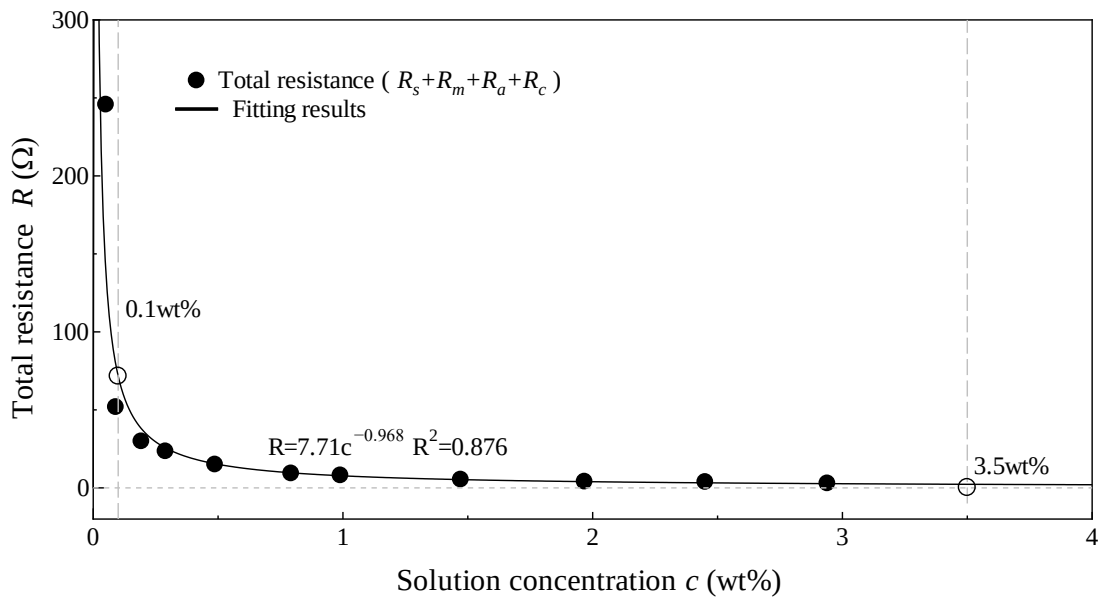


Fig. 4-11 Change in solution resistance and galvanic current density with the change in NaCl concentration.

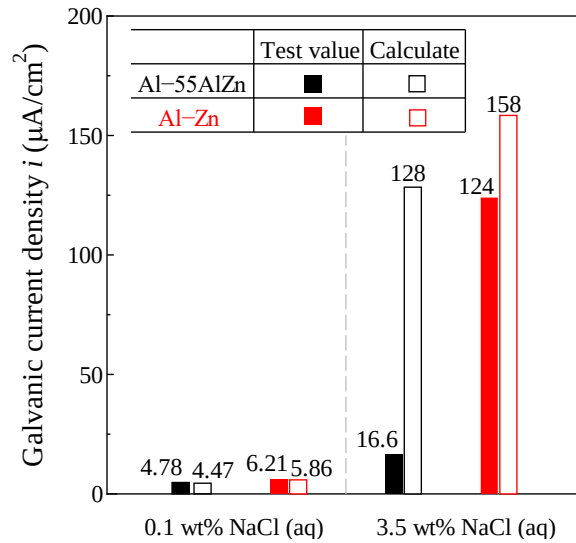


Fig. 4-12 Galvanic current density in 0.1 wt% and 3.5 wt% NaCl solutions.

Moreover, the galvanic current was in the initial stage, and it was not affected by the corrosion products. In the 0.1 wt% NaCl case, the galvanic current density of the test and the theoretical values were similar. Conversely, when in the 3.5 wt% NaCl solution, the test and the theoretical calculation exhibited a significant difference, especially, the 55Al-Zn and Al circuit. This circuit also had a lower current density than the Zn and Al circuit. This indicates that the 55Al-Zn coating has better performance in practical applications. To explain this, the following research was conducted. The appearances of the specimens before and after the electrochemical process are shown in Fig. 4-13. The images after the test show that there were many corrosion products on the surface of the electrode. The shielding effect of corrosion products can also reduce the corrosion speed of the galvanic current density [72]. Simonkollite was observed after the electrochemical test, and these corrosion products proved to have a better shielding effect [59,82]. The XRD results also proved that the materials were found in the exposure test. It is speculated that corrosion products can also provide a protective effect in the atmospheric environment. Li and Tachibana et al. studied the corrosion behavior of Zn and other alloy coatings. This study showed that the Zn coating had a significant weight loss and corrosion depth compared with the 55Al-Zn coating. This suggests that the Zn coating deteriorates easily [36,83]. The zinc coating is easily oxidized at ambient temperature, and the oxide film on zinc becomes sufficiently thin owing to deterioration [14]. The anodic dissolution of Zn

always occurs below the ZnO layer [84]. A schematic of the electrochemical test setup is shown in Fig. 4-14. During the initial stage of the electrochemical test, the surfaces of the two electrodes were smooth and clean. The oxide film of the Al-based coating was ruptured by dissolution or bypass by the solution [14], and the galvanic current density continuously increased and reached its peak. As corrosion continued, the corrosion products accumulated in both the anode and cathode, and the current density decreased, reducing the corrosion speed. The corrosion products of the anode (55Al–Zn) were more significant than those of the cathode (Al), as shown in the images after the test. At a concentration of 0.1 wt% NaCl solution, the calculated and testing values were almost the same. It is speculated that, in the low-concentration solutions, the surface has fewer corrosion products, and the shielding effect caused by the corrosion products is not significant. Conversely, in the 3.5 wt% NaCl solution, the calculated value is substantially higher than the testing value. From the corrosion behavior after the the test, it was found that the corrosion behavior in the 3.5 wt% solution was more severe than that in the 0.1 wt% solution because a large amount of corrosion products accumulated on the surface of the specimens. The corrosion products reduce the corrosion speed and cause a difference between the calculation and testing values. This behavior occurs particularly in the galvanic corrosion of 55Al–Zn and Al coatings.

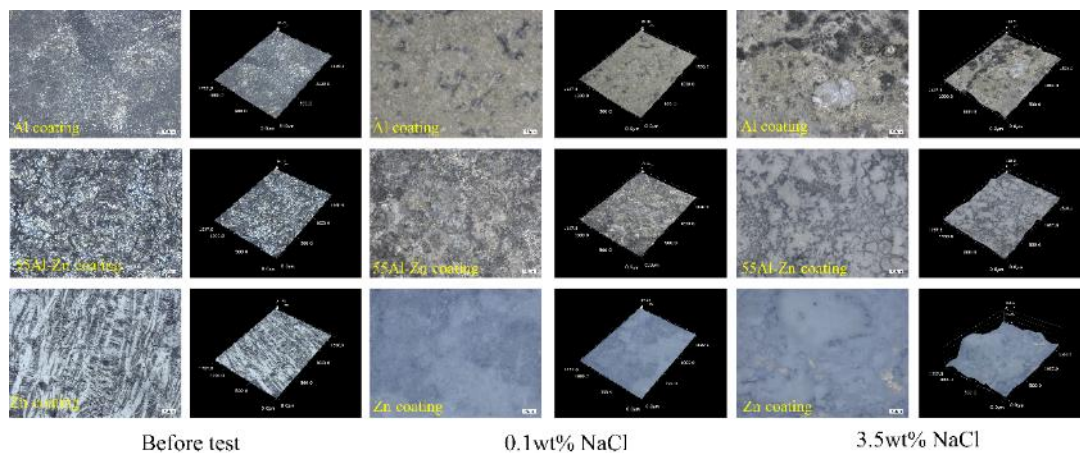


Fig. 4-13 Observation of the surface before and after the electrochemical test.

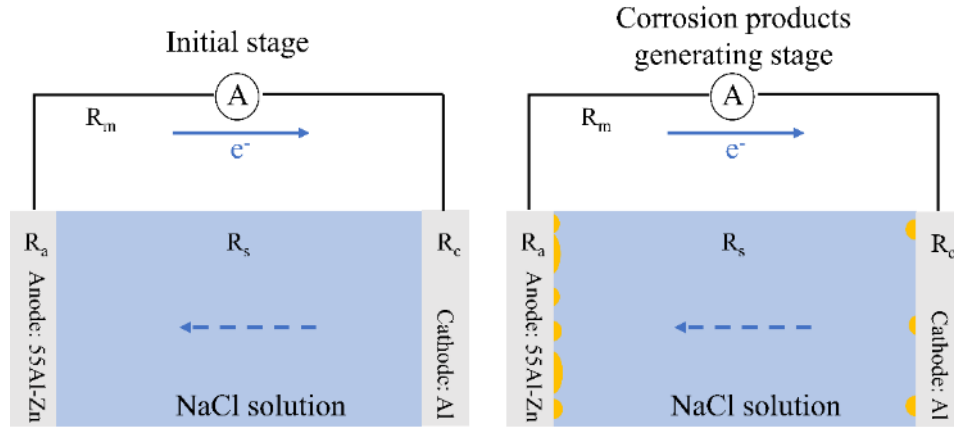


Fig. 4-14 Schematic of the galvanic corrosion during the electrochemical test.

The quantity of electric charge corresponds to the electron flow through the cathode during the electrochemical test. It was characterized to evaluate the speed of galvanic corrosion. The amount of charge is obtained by the integrating current and time. The amount of electric charge can only explain the total electric charge between different metals. The mass loss of the anode metal during galvanic corrosion is an accurate parameter for evaluating the effect of galvanic corrosion on the anode metal. There is a relationship between the quantity of electric power and mass loss. Corrosion loss is defined by the electric quantity (Q), which is calculated by integrating the instantaneous current and time. The equation, according to Faraday's law [85,86], is as follows:

$$\text{Quantity of electric charge } (Q) = \int_0^t i dt \quad (3)$$

$$\text{Mass loss (m)} = \frac{Q \cdot M}{n \cdot F} = \frac{\int_0^t i dt}{n \cdot F} \quad (4)$$

where i is the instantaneous corrosion current, t is the test time, M is the atomic weight of the metal, n is the number of valency, and F is Faraday's constant (96485 C/mol). In this method, the theoretical mass loss can be calculated using this equation [85,87]. In this study, we investigated the galvanic corrosion behavior of 55Al-Zn and Al coatings. Galvanic corrosion easily occurs when the Zn coating contacts the Al coating. In this case, Zn acts as the anode and Al as the cathode. To compare the galvanic corrosion behavior of the 55Al-Zn and Zn coatings, the same electrochemical test was performed. The mass

loss was calculated based on the galvanic current obtained from the previous electrochemical test. The results showed the total metal loss of the anode over a year in an aqueous solution environment. The changes in mass loss at different area ratios and concentrations of the NaCl solutions are shown in Fig. 4-15. K is the value of the slope factor, which reflects the change in mass loss with the change in the area ratio. The area of the anode (55Al–Zn coating) was constant (8 cm^2). The area of the cathode was always changed to 1, 2, 3, and 4 times larger than the anode area. The area of mass loss in this test was calculated based on the anode area. The correlation coefficient R^2 was used to study the degree of linear correlation between the variables. In this test, the correlation coefficient of the data of the four groups was greater than 0.95. Therefore, the results had a high positive correlation [88]. The results showed the change in mass loss with the area ratios varied in the following order: $K_{\text{Zn-coating}}(3.5 \text{ wt}\%) \gg K_{55\text{Al-Zn}}(3.5 \text{ wt}\%) > K_{\text{Zn}}(0.1 \text{ wt}\%) > K_{55\text{Al-Zn}}(0.1 \text{ wt}\%)$. In particular, the galvanic corrosion of the Zn coating in the 3.5 wt% NaCl solution was more severe than that in the other three situations. The concentration of the NaCl solution has a more significant effect on the galvanic corrosion of the Zn coating. The mass loss of the Zn coating in a high concentration NaCl solution showed obvious growth. Conversely, the 55Al–Zn coating exhibited a small mass loss compared with the Zn coating regardless of the concentration level (high or low) of the NaCl solution. These results were the theoretically calculated from the values of galvanic corrosion in the solution environment. In the atmospheric environment, the rain-washing effect can cause a water accumulation environment, but the wind and water vapor evaporation effects can also form a dry environment. Hence, in an atmospheric environment, galvanic corrosion speed and mass loss are much slower than those in an electrochemical test environment. However, the effect of the area ratio and concentration of the NaCl solution has a certain regularity. The electrochemical tests indicated that the Zn coating was more sensitive to the concentration of chloride ions. The galvanic corrosion current was much higher than that of the 55Al–Zn coating. Generally, 55Al–Zn has a better corrosion resistance when it is in contact with the Al coating compared with the traditional Zn coating.

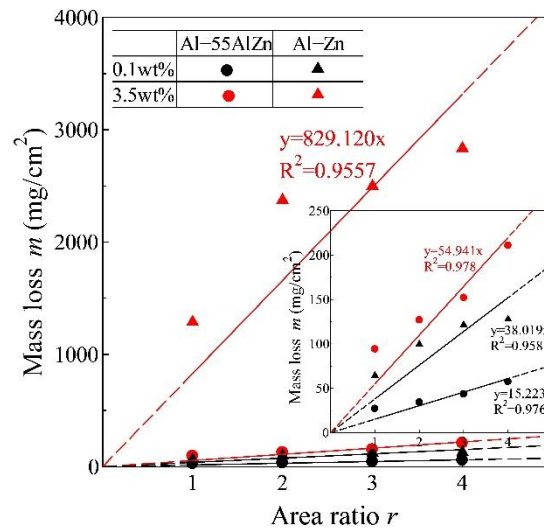


Fig. 4-15 Change in mass loss with different area ratios.

4.4 Corrosion behavior of hot-di aluminum coating in the atmospheric exposure test

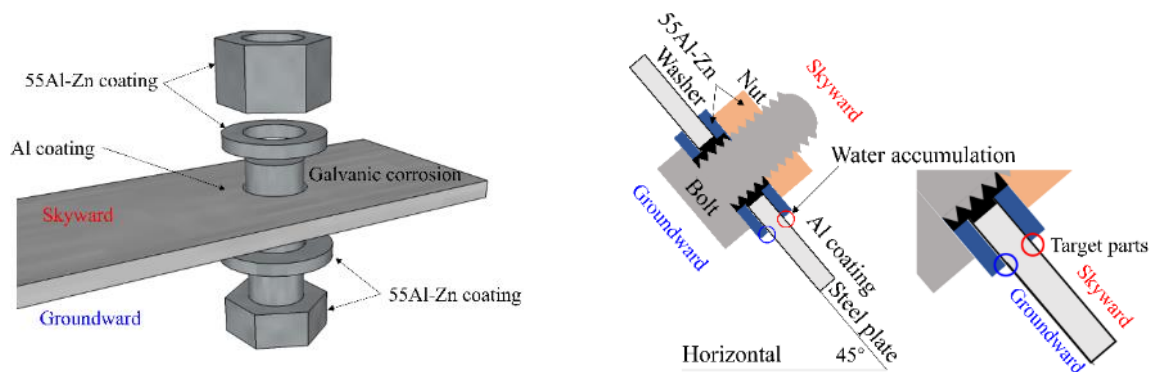


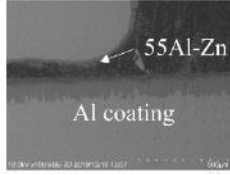
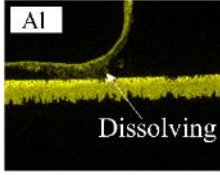
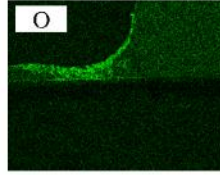
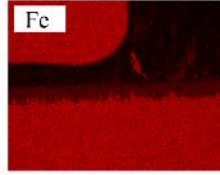
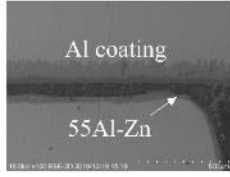
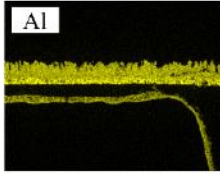
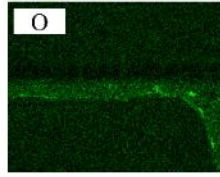
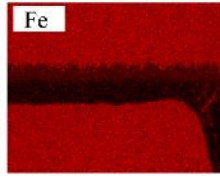
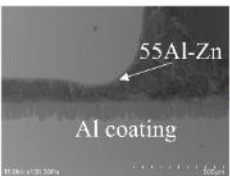
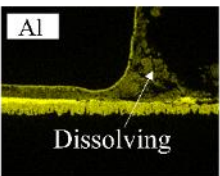
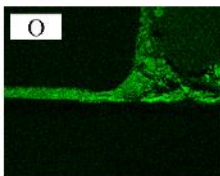
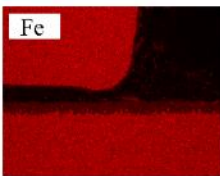
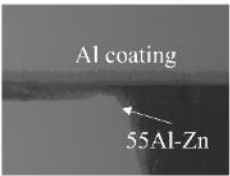
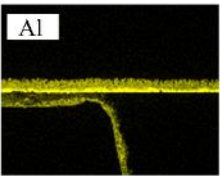
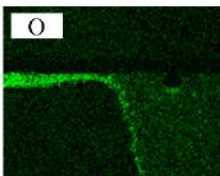
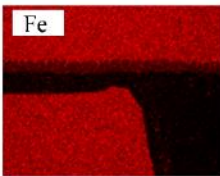
Fig. 4-16 Schematic and cross-section of the exposure test.

A schematic and cross-section of the exposure test are shown in Fig. 4-16. In the exposure test, the washer and steel plate coatings were made of different metals. The specimens were placed on the test racks at an angle of 45° . In places with a rain-washing effect, the lower part of the contact surface more easily accumulates water and forms a corrosive environment. Therefore, the part that deteriorated most easily was selected as the target. However, at the position that did not have the rain-washing effect, the airborne accumulation behavior of the skyward portion was more severe than that of the groundward portion. In this situation, the corrosion behavior of the skyward portion was

more serious because chloride is the main factor for the corrosion of metals in an atmospheric environment. In this study, the same parts of two exposure sites were investigated for comparison.

The deterioration of the different metal coatings caused by galvanic corrosion appeared on the bolted joint part. Table 4-3 presents the elemental distributions of UR (55Al–Zn bolt, Al steel plate, exposed at the University of the Ryukyus) and KY (55Al–Zn bolt, Al steel plate, exposed in Kyoda) obtained using EDS. Corrosion products were produced in both the skyward and groundward portions, identified by the O element. A high concentration of O indicated that an oxide was generated by galvanic corrosion. According to the oxide products, the corrosion behavior of KY was found to be more severe than that of UR. The distribution of Al indicated that the corrosion behavior of the skyward portion was more severe than that of the groundward portion. For the specimen at UR, the water accumulation effect accelerated the galvanic corrosion owing to the rain-washing effect of the lower part in the skyward portion. A dissolution behavior of Al on the ground for the specimen at UR was not obvious. For the KY specimen, the dissolution of Al occurred at both skyward and groundward positions. With respect to the distribution area of Al, the skyward area exhibited a more severe influence than the groundward portion. The KY specimen did not exhibit a rain-washing effect; therefore, airborne salt was the main factor influencing the corrosion behavior. A high chloride concentration accelerated the dissolution of Al and galvanic corrosion. In addition, the distribution of Fe indicated that the steel was not corroded, and it was well protected. Thus, the washing effect on the surface of the coating removed a large amount of chloride, which reduced the corrosion rate of the metal coating. Most metals and alloys lead to the same conclusions [15]. According to the four years atmospheric exposure test, galvanic corrosion can occur easily in regions with both water accumulation and a high concentration of chloride. A typical characteristic of galvanic corrosion is the dissolution of metals, which leads to a decrease in the thickness of the protective coating and finally, elimination of the shielding and cathodic protection. Elemental analysis mapping showed that for the 55Al–Zn coating, the dissolution behavior of the part with high concentration of chloride was more severe than that with water accumulation. Galvanic corrosion of the 55Al–Zn coated washer and Al-coated steel plate was observed.

Table 4-3 Elemental distributions in UR and KY specimens on the cross-section perpendicular to the front surface.

55AlZn (Bolt), Steel plate (Al)	UR	Skyward				
		Groundward				
	KY	Skyward				
		Groundward				

A gap existed between the washer and the steel plate, and galvanic corrosion occurred on the outside part of the bolt-jointed part. Crevice corrosion occurring on the gap is unknown. The element distributions on the cross-section of the outside and interlining parts are shown in Fig. 4-17. Al dissolution behavior was observed on the outside. A higher oxide content can be found on the Al dissolving parts, indicating that part of the 55Al-Zn coating has deteriorated into another substance. Although galvanic corrosion occurs outside, the corrosion behavior is not obvious. Galvanic corrosion had little effect on the surface of the 55Al-Zn coating and the steel substance was then complete. This also indicated that galvanic corrosion between the 55Al-Zn and Al coatings was not significant. The interlining part was near the outside part and on the crevice between the washer and steel plate. To verify whether crevice corrosion occurred, the interlining part was observed using SEM-EDS. The results illustrated that the Al coating was complete because of the outermost Al layer, and the intermetallic Fe-Al layer could be clearly observed. A deterioration behavior of the 55Al-Zn and Al coatings was not observed. The

oxide content was then low. The galvanic corrosion behavior only occurred on the outside, and the corrosive environment could not permeate the gap.

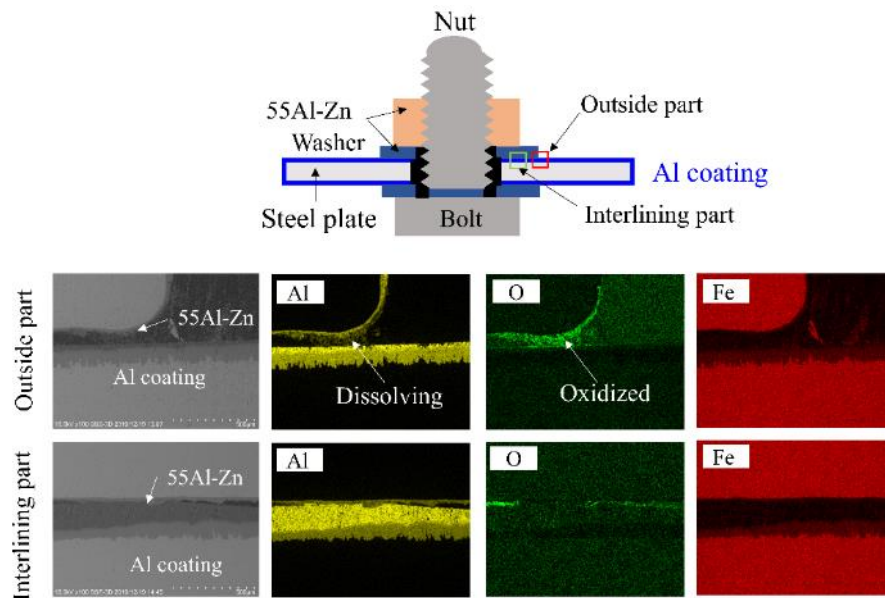


Fig. 4-17 Element distribution obtained by SEM-EDS on the cross-section of the outside and interlining parts.

4.5 Summary

The galvanic corrosion in hot-dip Al and 55Al-Zn coatings was studied. The conclusions of this chapter can be summarized as follows:

- (1) In the electrochemical test, with an increase in the area ratio ($S_{Al}/S_{55Al-Zn}$) of the cathode (Al) to the anode (55Al-Zn), the galvanic current exhibited a significant linear growth relationship. Although the galvanic current increased immediately after immersion in the electrolyte, it also decreased after a certain period.
- (2) The current densities of galvanic corrosion of the 55Al-Zn and Al coatings in the electrochemical tests were significantly lower than the theoretical value without considering the effect of corrosion products. The XRD analysis of the surface of the 55Al-Zn coating after the electrochemical test confirmed the formation of protective corrosion products.
- (3) The corrosion products generated on the 55Al-Zn coating by galvanic corrosion after the atmospheric exposure test were the same as those identified in the electrochemical test.

From these results, it is expected that the 55Al-Zn coating will maintain its integrity in the long term because of the protective properties of the corrosion products generated in the initial stage. Therefore, it was confirmed that there is no concern regarding anomalous corrosion in joints between 55Al-Zn coating bolts and hot-dip Al-plated members in steel structures used in atmospheric environments.

CHAPTER 5 CORROSION BEHAVIOR OF HOT-DIP ALUMINUM COATING CONTACT WITH CONCRETE

5.1 Introduction

Concrete is the most widely applied construction material in various infrastructures [91,108,109]. The concrete pore solution keeps a strong alkaline medium due to the amount of calcium hydroxide filling in the concrete pore in the process of the hydration reaction of cement. pH is an important parameter to indicate the alkalinity level of concrete. The pH of ordinary Portland cement concrete is between 12.5 to 13, but it can decrease due to deterioration mechanisms such as chloride ingress, carbonation, or acid attack [110,111]. In this alkaline environment, the surface of the rebar can form a stable passive film, which provides good protection to the rebar against corrosion. However, the passive film of rebar becomes unstable and deterioration in the effect of carbonation and chloride ingress. There is a certain value on the pH and Cl⁻ concentration in concrete, above that the corrosion risk is high. The corrosion of rebar embedded in concrete not only demolishes the bonding force between the rebar but also leads to cracks in the concrete due to the volume expansion of corrosion products [22,112]. Moreover, the zinc and epoxy-coated rebars have been applied as anti-corrosion reinforced rebars into concrete in high chloride or another heavy corrosive environment [26,57,113]. Al and Al-based coatings are widely used in automobile engines and construction materials as an alternative to zinc coating to reduce the weight, improve the mechanical properties, and have a better high-temperature oxidation resistance behavior [26,114]. Steel is dipped into the molten Al metal, and the interdiffusion of the Al and steel appears and finally leads to the formation of different intermetallic. For the hot-dip Al coating, the coating consists of the outermost pure Al coating and Fe-Al intermetallic layer. This layer is about 100μm, the material properties are brittle. The intermetallic layer comprises an outer FeAl₃ layer and inner Fe₂Al₅ layer. The Fe₂Al₅ is the main factor of the coating phase and final coating properties [37,38]. Hot-dip Al-coated mild steel has been widely used in high-temperature environments due to the formation of fine and dense Al₂O₃ with good oxide resistance on the surface of mild steel. The corrosion resistance also contributed to the formation of this

thin and stable oxide film [23,43]. Nowadays, the corrosion behavior of zinc and epoxy-coated rebar and steel structures has been studied in-depth [115]. In this field, the corrosion behavior of Al coating-related research is not clear, especially the corrosion behavior of Al coating and concrete. Hot-dip coatings can be used for automobiles, vehicle exhaust systems, domestic appliances, fences, platforms, and some accessory parts of structures. The hot-dip Al-coated fence contact with concrete in the actual situation is shown in Fig. 5-1. In this situation, Al coating contact with concrete directly, the condition of long-term use is unknown. In this research, we focused on the study of the corrosion behavior of hot-dip Al coating and concrete, the first stage is to study whether hot-dip coated steel bars can be embedded in fresh concrete. The other topic is the contact corrosion behavior of hot-dip Al-coated steel members and hardened concrete. So corrosion behavior of hot-dip Al coating related to concrete can be explained.



(a) The ladder coated by hot-dip Al coating (b) Hot-dip Al coated steel plate contact with concrete

Fig. 5-1 The contact of hot-dip Al coated steel member and concrete in the actual situation.

5.2 Corrosion behavior of hot-dip aluminum contact with fresh concrete

The round steel bar ($\Phi 12\text{mm}$, length: 30mm) and steel plate ($60 \times 60 \times 12\text{t mm}$ JIS G 3106 SM490A) were coated by hot-dip Al coating. The thickness of the Al coating is about $120\text{ }\mu\text{m}$ measured by the electromagnetic film thickness gauge. The steel substrates were coated after the typical surface treatment consisting of degreasing, pickling, and fluxing. The concrete compositions of this study are shown in Table 5-1. The round steel

bar specimens were immersed into the fresh concrete to evaluate the intensity of the Al coating reaction with the alkaline environment of concrete. Meanwhile, study the bonding force between the rebar and concrete.

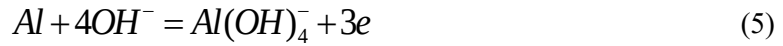
Table 5-1. Concrete compositions (kg/m³)

Test type	Water	Cement	Sand	Gravel	w/c ratio
Fresh concrete	290	579	1304	0.00	0.50
pH measurement, Exposure test	154	285	783	1087	0.54

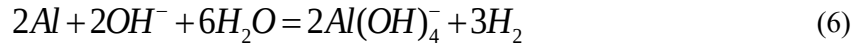
Rebars coated by zinc coating have been proven to be an effective method against corrosion attacks. Hot-dip Al-based coating is a new generation of alternatives for zinc coating due to its better corrosion resistance behavior. Whether the hot-dip Al coating can be used for the rebar protective coating is not clear. Al is a special metal that can react with acid and alkaline media. Concrete in the hardening process has a high pH level, whether Al coating can be dissolved in the moist mortar environment can be verified by this test. In this test, the concrete was injected into the stainless thimble (Φ 100mm, Height: 200mm JIS A 1132), and the round bar (Φ 19mm, Length: 100mm JIS G 3101 SS400) consisted of two groups. 1) The round steel bar was coated by Al coating. 2) The round bar was after blast treatment (ISO8501-1 Sa2.5) by abrasive (Al_2O_3 , Moh's hardness: 12, JIS grain index: 57.8, special gravity: 4.0). Two groups of specimens were inserted into the concrete. The bare round steel bar was set for a contrast group. The immersed part of the round bar is about 70mm, and the remaining 30mm is exposed to the laboratory atmosphere. In this test, the mortar consisted of water, cement, and sand. Gravel was not added to the mortar to have a clear observation of the round bar interface.

The round steel bar was immersed into the mortar after 8 weeks. The cross-section examination was carried out on the specimens after cutting in the middle of the mortar. The visual inspection of the round bar specimens is shown in Fig. 5-2. For the ordinary round bar after blast treatment, the bonding condition of the round bar and mortar is very well, air bubbles can't be found on the interface surface. In this situation, the fresh mortar is in contact with the abrasive materials. However, the Al-coated round bar has different

results. Some small air bubbles can be inspected on the interface of the round bar and mortar. The bubbles are the hydrogen caused by the reaction of Al coating and an alkaline environment. The OH^- ions in the alkaline media are the reason for Al dissolution on the surface. As a result of hydration, dissolution, and change the film structure of Al. The overall anodic reaction that takes place in the corrosion of aluminum in alkaline solution can be denoted below[116–119].



and the overall main reaction taking place at the Al surface can be shown by the following equation:



The formation of aluminate comes from the anodic film of the electrode surface. The results indicated that the hot-dip Al-coated steel bar can't be used for the rebar in the fresh concrete, the fresh concrete environment can lead the Al coating layer to dissolve. The dissolution of Al coating between round steel bars and concrete not only decreases the bonding force but also leads to cracks in the concrete due to the volume expansion of corrosion products[120]. The cracks continue to accelerate the mass transport of the corrosion process, and serious corrosion leads to safety issues and the bearing capacity of constructions in the end.

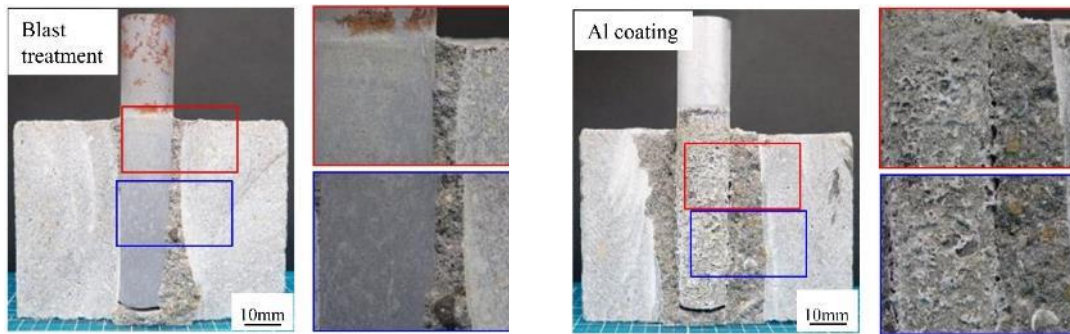


Fig. 5-2 Interface cross section observation of round bar and mortar.

The round bar specimens coated by Al coating were used for OCP measurement. The specimens were immersed into the $\text{Ca}(\text{OH})_2$ aqueous solution. The temperature was about $20 \pm 2^\circ\text{C}$, the electrolyte was exposed to the laboratory air and without any stir [121]. The initial pH of the electrolyte was about 12.6, the changing of the pH was adjusted by adding pure water. The measurement range of pH was from 10.25 to 12.6. The Al-coated

specimens were the working electrode. The Ag/AgCl electrode in the saturated KCl electrolyte was used as the reference electrode. The OCP measurement was performed by a potentiostat (Princeton applied research). Variations of OCP with pH changing for un-exposed and un-corroded Al are shown in Fig. 5-3. The positive shift of OCP is mainly due to the formation of the native oxide layer on the substrate in the early stage. However, OCP shifted negatively showing general damage to the native oxide layer. Finally, the oxide layer is damaged, and the corrosion rate of the Al coating is accelerated. S. Adhikari et al. in their research on the anodic dissolution of Al in alkaline solutions indicate that at pH 11, the behavior of the Al is similar to that in neutral pH solutions [10,75,91]. The potential at the metal/film interface indicates that the primary anodic reaction is the Al oxidation. In this case, the oxide film is still complete and can provide a protection effect against the corrosion environment [122]. When the pH is near 12, the surface film resistance is significantly decreased, and the dissolution current becomes larger due to the decrease in ohmic resistance [123,124]. A pH over 12, tends to lower conduction resistance and higher water permeability than the film at a lower pH value. This indicated that when the pH is over 12, the oxide film is damaged and Al dissolution behavior occur and become more obvious.

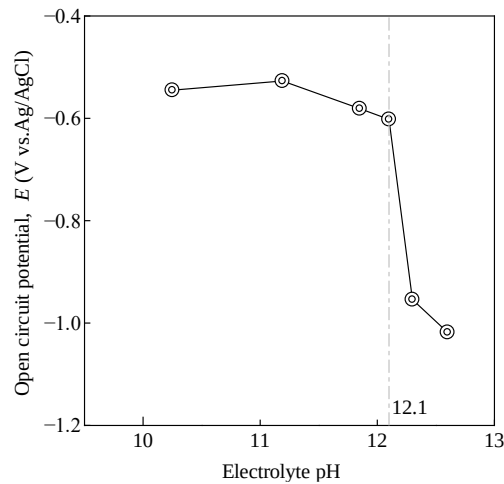


Fig. 5-3 The variation of OCP with the change of pH for the Al coating.

5.3 The pH changes of concrete during the hardening process

The concrete was injected into the stainless thimble, and the temperature of the

laboratory was about 20°C. After 24 hours, the specimen was placed into the constant temperature and humidity cabinet (20°C, 100%RH, Espec Corp.) for about 28 days, a polyethylene thin film was covered on the surface of the specimen to keep moisture. pH is an important parameter to evaluate the alkalinity of concrete. The surface pH value of the concrete was measured by a pH meter (0040-10D, Laqua Horiba Inc.) during the hardening process.

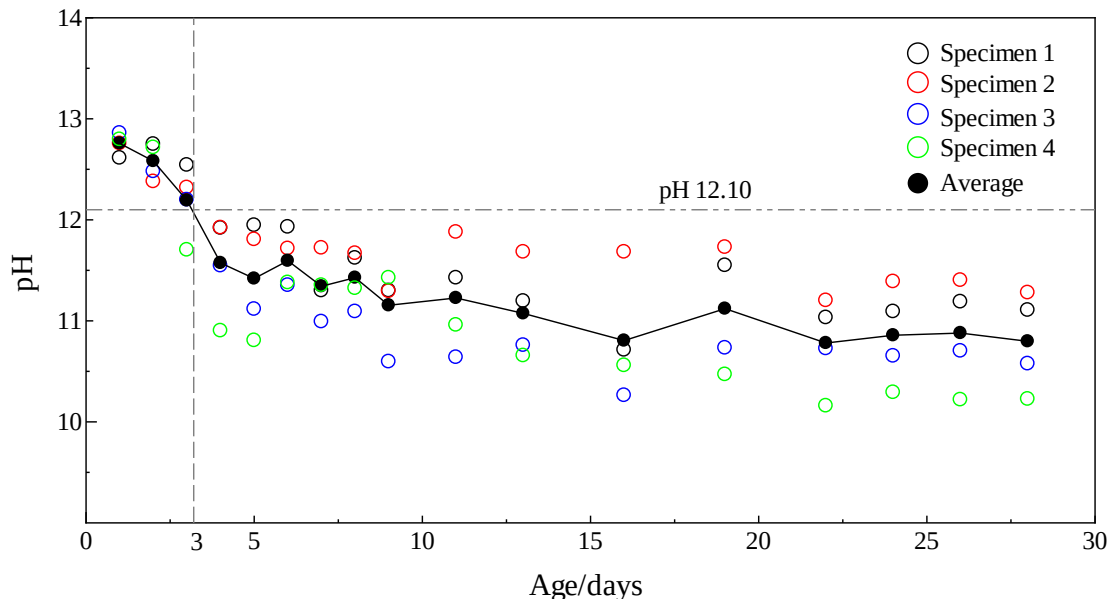


Fig. 5-4 The pH changes with the curing age.

The pH value on the surface of the concrete was measured during the hardening process. On the period of 28 days, 4 groups of specimens were taken and got the average value. The pH change with time is shown in Fig. 5-4. From this trend curve, the pH decreased significantly in the initial stage. In the early three days, the average pH value was higher than 12.1. After the first three days, the concrete has become hardened completely, and the pH of the concrete trended to stable. From the results obtained from the OCP measurements, the conclusion can be described that in the early three days, the pH value was over 12.1. In this case, the Al coating can be dissolved in the fresh concrete mortar. As the hardening process, the pH value drop at the early stage is due to the diffusion of hydrogen and hydroxide ions which is attributed to the difference in their concentrations [91]. This test indicates that at the early stage, hot-dip Al coating can't play a role in a better corrosion resistance behavior, the coating can be dissolved in a

highly alkaline environment and can't be applied in fresh concrete.

5.4 Analysis of hot-dip aluminum coating after atmospheric exposure test

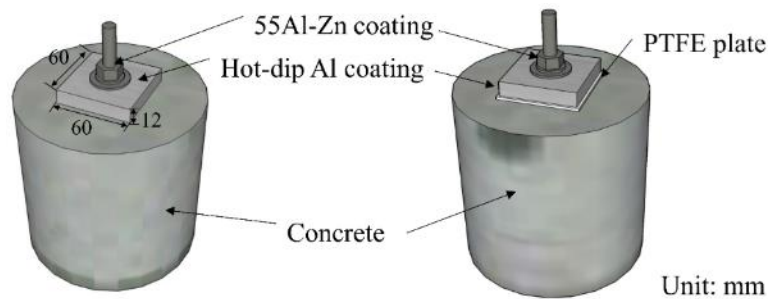
To evaluate the corrosion behavior of hot-dip Al-coated steel members and hardened concrete in the atmospheric environment, the exposure test was carried out. The steel plates (JIS G 3106 SM490A) coated by Al coating (thickness is about 120 μ m) with the concrete base have been exposed at Kyoda (26°32'N, 127°57'E donated as KY), Univ. of the Ryukyus (26°14'N, 127°45'E donated as UR) and Kyushu Univ (33°35'N, 130°13'E donated as KU). The exposure period is from June 2019 to Nov. 2021 about 2.5 years. The specimens were placed horizontally on the plastic foundation support, the scene of the exposure test was shown in Fig. 5-5 (a). The average environment data measured from 2013 to 2022 are shown in Table 5-2. The schematic diagram of the exposure test is shown in Fig. 5-5 (b).

Table 5-2. Atmospheric environment of Kyoda (KY), University of the Ryukyus (UR), and Kyushu University (KU) sites.

Exposure site	Temperature T (°C)	Relative Humidity RH (%)	Airborne salt w (mdd)	Offshore distance (m)	Average precipitation (mm/day)	Rain washing effect
KY	21.8	84.7	0.5	30.0	5.3	Without
UR	22.9	81.9	0.3	2,300	5.2	With
KU	17.3	76.9	0.5	2,900	6.2	With



(a) The scene of specimens in the exposure site.



(b) The schematic diagram of the specimen.

Fig. 5-5. The scene and schematic diagram of specimens in the exposure site.

The specimens were exposed in three exposure sites (KY, UR, KU). Although the hot-dip Al can't be used in fresh concrete, it can be used in place of hardened concrete still needs to be studied. The steel plate coated by hot-dip Al coating was fixed on the surface of the hardened concrete base and exposed to the atmospheric environment for 2.5 years. The appearance of the specimens after a year of exposure is shown in Fig. 5-6. KY is the only exposure site that doesn't have the rainy washing effect, this place has a high airborne salt amount due to the cost and no-rainy washing environment. The high chloride causes the skyward of the specimens to have a serious corrosion behavior, some brown spots can be found on the surface of the skyward. Particularly, the corrosion products of Al were a white color, the brown spots indicated the corrosion had penetrated the outermost Al coating and reached the Al-Fe intermetallic layer. The brown spots are assumed that the element of the Al-Fe alloy layer continues to deteriorate. The contact part of Al coating in KY has a better condition and can't find any corrosion behavior. On the contrary, in the PTFE group, a certain range of corrosion behavior can be found, and the brown spots can be recognized by visual observation. After 2.5 years of exposure test, any corrosion behavior can't be found in the skyward on the UR and KU. This behavior illustrates that the rainy washing effect has a very significant effect on reducing of corrosion rate. The rainy washing effect can significantly move away a lot of chloride and corrosion substrates. However, the corrosion behavior of the contact part in the other sites is different from KY. The corrosion of the contact part is caused by the stagnant water effect. In a rainy washing environment, the crevice between the Al-coated steel plate may accumulate a lot of water. The stagnant water environment can't disappear immediately after the heavy rain. The water accumulated in the crevice is different from evaporation and dispersion. The stagnate water environment can continue to have a positive effect on the corrosion behavior of contact parts. It is the reason why the corrosion behavior of groundward is more serious than skyward in the rainy washing effect area. In this situation, the stagnated environment is not neutral, the rainy water will become the alkaline environment in the end by the effect of the concrete. We can compare the corrosion behavior of the contact part in three different exposure sites, the contact part of KY has a good surface condition compared with UR and KU due to hot-dip Al coating can contact

with concrete in a dry environment and will not have any tendency of corrosion in the nearly 2.5 years. Moreover, although the surface condition in the contact part of UR and KU is not as good as KY, the corrosion behavior in those two places also can't be found. The tarnishing of the surface is caused by the stagnant water environment. The PTFE groups in this test only let the hot-dip Al coating can't contact concrete directly. Hence, completely avoid the impact of concrete on the hot-dip Al coating. The PTFE sheet can prevent the penetration of rainwater. The slight corrosion behavior can be found on the surrounding area near the side, it may be caused by the accumulation of rainwater between

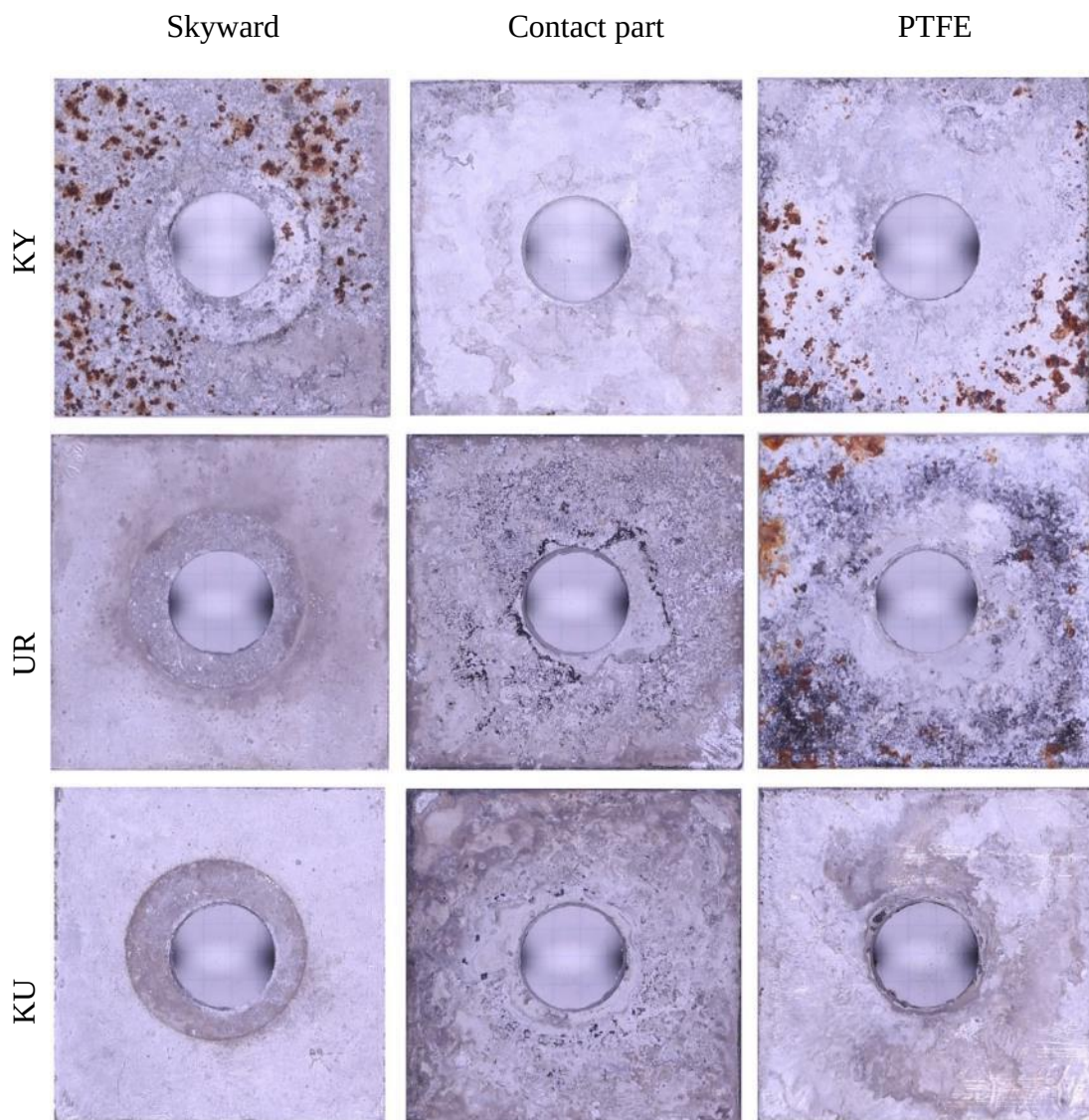
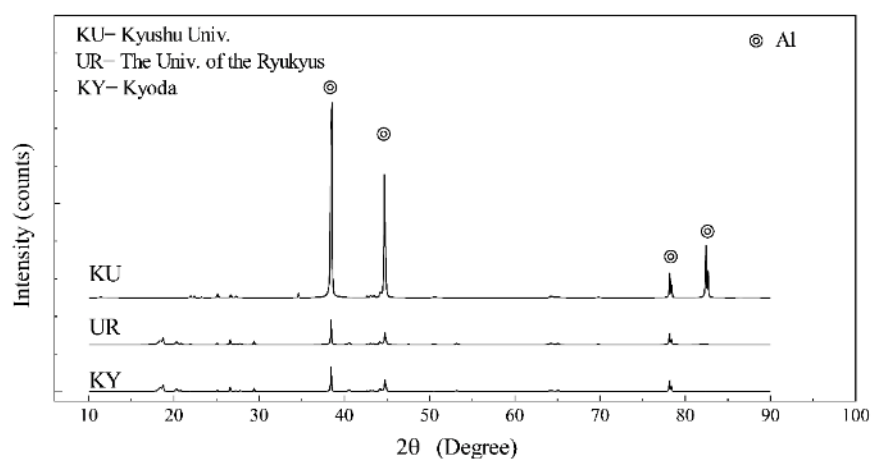
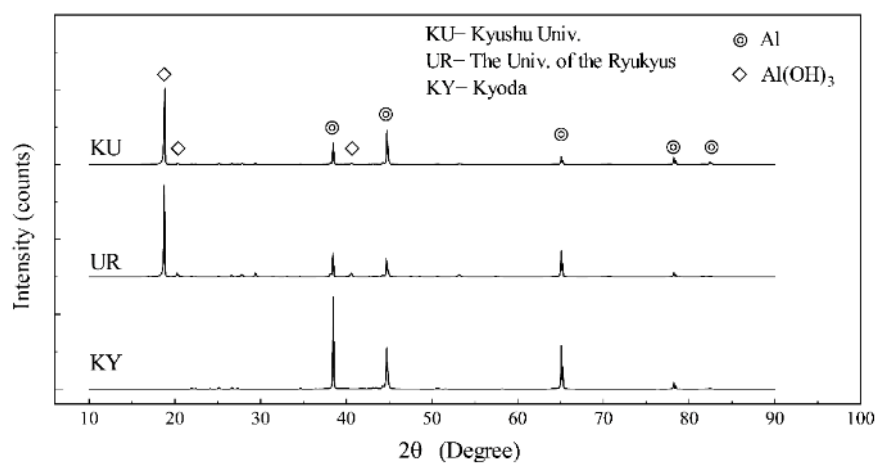


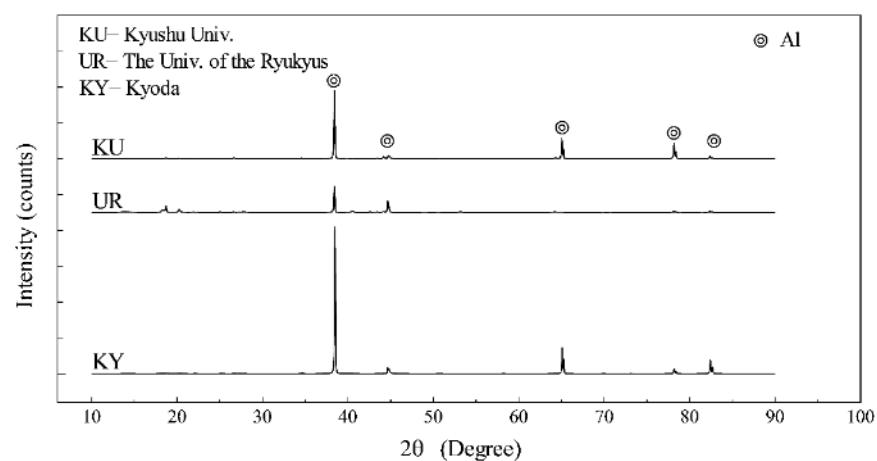
Fig. 5-6 Appearance of the exposed specimens after 2.5 years of exposure.



(a) skyward



(b) Contact part



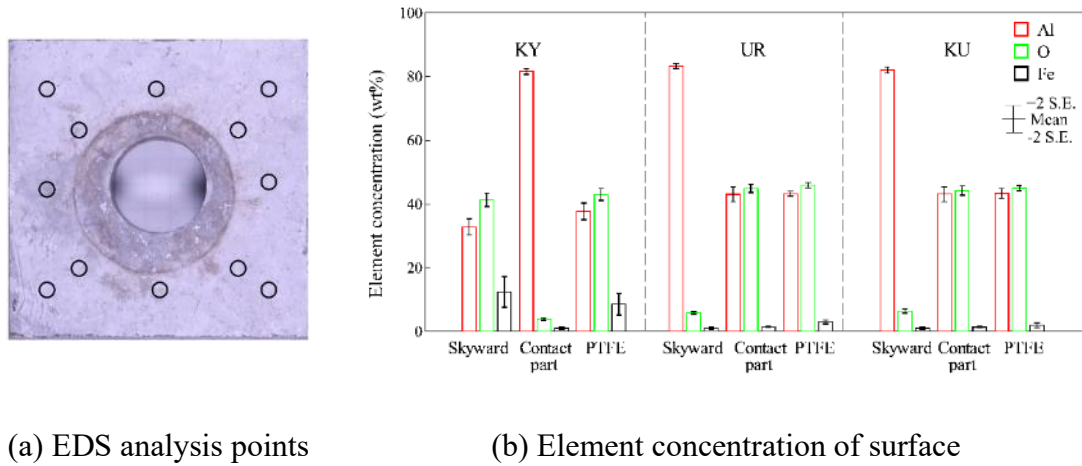
(c) PTFE

Fig. 5-7 The corrosion products analysis by XRD analysis.

the hot-dip Al-coated steel plate and the PTFE sheet. The test results indicated that the corrosion behavior of the contact part is not more serious than the PTFE case in the same exposure site. It can be concluded that hot-dip Al coating contact with contact whether it's in a dry or stagnant water environment also has a better corrosion resistance ability. The corrosion products formed on the surface were identified by XRD analysis. The XRD spectrums of the specimens exposed in KY, UR, and KU are shown in Fig. 5-7. From the skyward three exposure sites, only the peaks of Al metal were detected. The contact part of three exposure sites, the research focuses on the fully contact part, so the analysis area is near the fixed hole of the Al-coated steel plate. In the contact part of the KY exposure site, only Al metal was identified. Besides Al, the hydroxide can't be identified due to there being no rainy washing effect. In the contact part of UR and KY, the results are similar. Only the peaks of Al metal and hydroxide $\text{Al}(\text{OH})_3$ were detected on the surface of the contact part. The reason for hydroxide can be identified is due to the stagnant water environment. Although an Al oxide film is usually formed on the Al after atmospheric exposure, the contact part of UR and KY didn't have the peaks of oxide in the spectrum. This suggests the thickness of the oxide film may not much enough for the identified. The PTFE sheet group shows only Al can be identified by the XRD [100]. Although there is a certain corrosion behavior on the surrounding part near the side, the brown spots indicated that Fe can be seen, the nearly fixed hole part is perfect and corrosion behavior can't be found.

The corrosion is considered to be a random event on a uniform surface. We selected 12 points of a permanent position in different specimens used for the surface elements evaluation. The concentration of elements is an important parameter for an indication of deterioration. The average of 12 points was calculated as the surface element content. The surface element concentrations of skyward, contact part, and PTFE at three exposure sites are shown in Fig. 5-8. The error bar used 2 times the standard error. The higher concentration of Al and lower concentration of O indicated better surface condition and no corrosion behavior. The results indicated that, for the skyward, the corrosion behavior in KY is more serious than UR and KU. The concentration of Al is the lowest level among the three sites, the highest oxide concentration shows the deterioration of Al coating in KY is more serious. The reason is the higher airborne salt accumulation effect. We

compare the contact part of exposure sites, KY has the highest concentration of Al and the lowest concentration of O, and it declared that the surface condition of KY is better than UR and KU. The element concentration of the contact part in UR and KU has a similar situation. Meanwhile, we compare the element concentration of the contact part and PTFE side in the same exposure site. In KY, the corrosion behavior of PTFE is more serious than the contact part. On the contrary, the corrosion behavior of the contact part and PTFE in UR and KU have similar cases. In a word, the corrosion behavior of the contact part is no more serious than PTFE in three exposure sites. These results are also consistent with previous surface visual observations.



(a) EDS analysis points

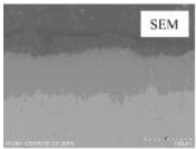
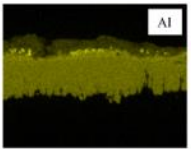
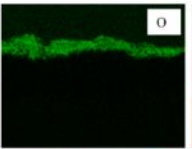
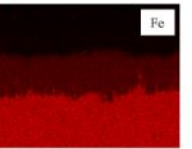
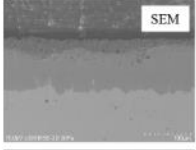
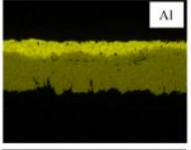
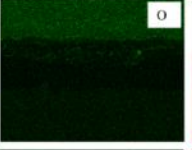
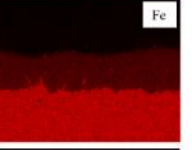
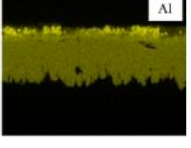
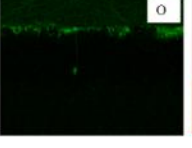
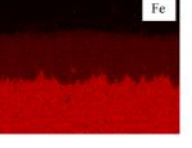
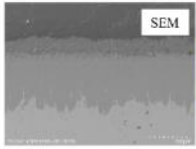
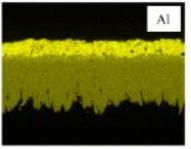
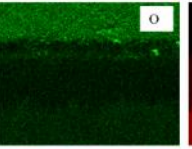
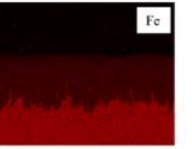
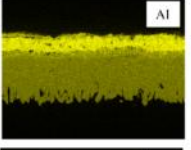
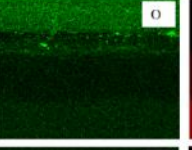
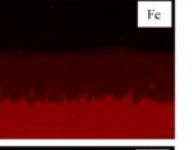
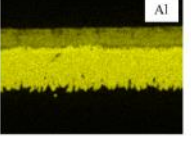
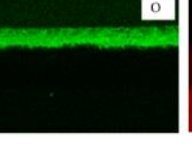
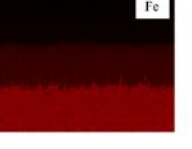
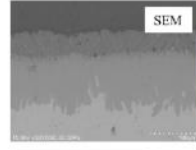
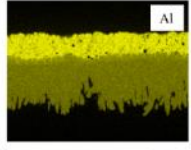
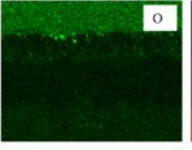
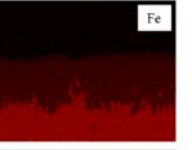
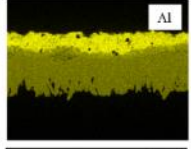
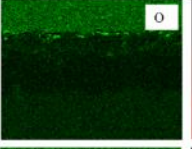
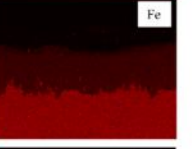
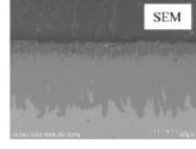
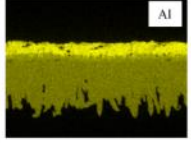
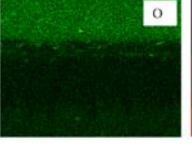
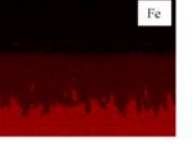
(b) Element concentration of surface

Fig. 5-8 The surface element concentration evaluation of the specimens after the exposure test.

From the surface element concentration analysis, the results stated that the corrosion behavior of the contact part is not more serious than PTFE. However, the XRD analysis also indicated the formation of hydrides on the surface of the contact part. To verify the surface condition of the contact part and PTFE, the cross-section was carried out. The SEM image and EDS analysis of the cross-section are shown in Table 5-3. KY, the observation part is the place where the brown spots occur in the skyward. From the EDS analysis results, the majority of Al coating has disappeared, and only some tiny parts still can be found. The outermost Al layer causes pitting corrosion, the pitting spreads downward. The pitting corrosion has spread to the Al-Fe alloy layer. The brown spots that were guessed before can be confirmed to be Fe elements. The brown spot part has pitting

corrosion the other part of skyward also has a better complete layer. However, in the high

Table 5-3. SEM image and EDS analysis of cross section after exposure test.

KY	Skyward				
	Contact part				
	PTFE				
UR	Skyward				
	Contact part				
	PTFE				
KU	Skyward				
	Contact part				
	PTFE				

chloride concentration environment, the pitting corrosion still occurs on the small area of the part. The majority of the parts have a better and complete condition. The contact part of KY, the outermost Al layer is still very perfect. In this condition, the Al coating has better durability. The corrosion behavior of UR and KU are very similar. The skyward of UR and KU, after the atmospheric exposure test, the surface of the specimens is still complete, and can't find any corrosion behavior. This indicated that the rainy washing effect has a lot of advantages to corrosion resistance. In the contact part of UR and KU, the corrosion behavior was not obvious, only the thick oxide layer can be found on the surface of the outmost Al layer. From the SEM-EDS analysis, the corrosion behavior in the contact part of KY, UR, and KU can't be observed. The utmost Al layer of all three exposure sites is very complete. It can be considered that almost no corrosion occurred in the contact part of them. We compare the corrosion behavior of the contact part and PTFE in the same exposure site. The results show the corrosion behavior of the contact part is not more serious than PTFE.

5.5 The corrosion behavior of Al coating contact with concrete

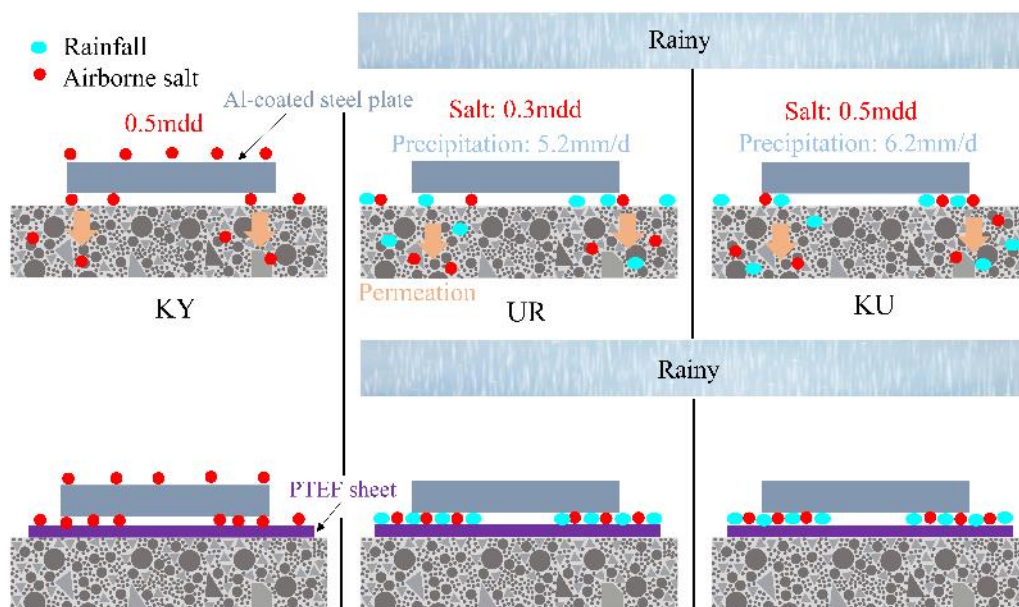


Fig. 5-9 The corrosion behavior of Al-coated steel plate contact with concrete.

The corrosion behavior of Al coating contact with concrete is shown in Fig. 5-9. In

KY, there is no rain washing effect and it is very close to the sea, leading to a very large amount of salt concentration. In this case, the corrosion of the empty surface is relatively obvious, meanwhile, in the contact part no corrosion behavior can be found. This means, hot-dip Al coating contact with concrete directly in the dry environment. The concrete doesn't cause the corrosion of the Al layer. In UR and KU, the condition is different from KY. Due to rain washing, the corrosion of the empty surface is relatively less, and the corrosion of the contact part is a little bit more obvious than the dry environment in KY. Due to the rain washing effect, rainwater will enter along the cracks between the Al-coated steel plate and the concrete. The stagnant water environment will cause a little corrosion behavior on the surface of the contact part. From the cross-section analysis results, although in the stagnant water environment, the corrosion behavior almost can't be found. The group of PTFE specimens is completely out of touch with concrete, comparing the corrosion behavior of contact and non-contact with concrete. The corrosion behavior of the contact case is no more serious than the PTFE case. This suggested that the corrosion behavior of Al coating contact with concrete is not serious and can be used for long-term application.

In UR and KU, the condition is different from KY. Due to rain washing, the corrosion of the empty surface is relatively less, and the corrosion of the contact part is a little bit more obvious than the dry environment in KY. Due to the rain washing effect, rainwater will enter along the cracks between the Al-coated steel plate and the concrete. The stagnant water environment will cause a little corrosion behavior on the surface of the contact part. From the cross-section analysis results, although in the stagnant water environment, the corrosion behavior almost can't be found. The group of PTFE specimens is completely out of touch with concrete, comparing the corrosion behavior of contact and non-contact with concrete. The corrosion behavior of the contact case is no more serious than the PTFE case. This suggested that the corrosion behavior of Al coating contact with concrete is not serious and can be used for long-term application. To assess different atmospheric environments, the ordinary low carbon steel specimens (SM490A 150×70×6t mm) were exposed to the KY, UR, and KU exposure sites. The corrosion condition of this test in each exposure site was the same as the exposure test of Al coated steel plate contact with concrete. The specimens were oriented towards the ground at a

45-degree angle from the horizontal direction. After four years of atmospheric exposure tests, the corrosion depth over time is measured by the weight loss method. The mean corrosion depth of specimens with exposure time is shown in Fig. 5-10. The data were fitted to a linear relationship and through the origin of coordinates. From the results, it can be seen that the corrosion depth of KY is significantly greater than that of UR and KU. Among them, the corrosion depth in KU has the lowest growth. In this study, although the corrosion behavior of non-contact case is more serious than direct case, the corrosion behavior of KU is no more serious as that of KY and UR due to the corrosion environment of KU is relatively milder compared to KY and UR.

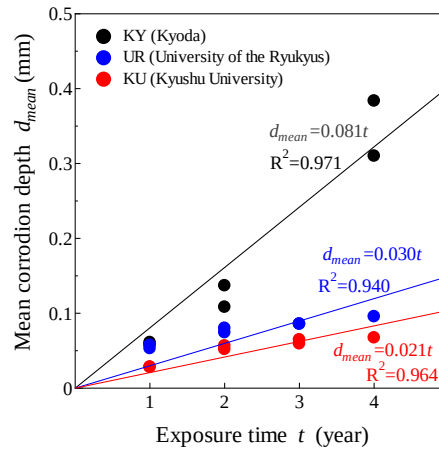


Fig. 5-10. The mean corrosion depth with time in different exposure sites.

The corrosion process of Al coated steel plate in contact with concrete is shown in Fig. 5-11. In an atmospheric environment that has airborne salt and without rain washing effect, when the Al coated steel plate contact with concrete directly, the airborne salt will enter the crevice between Al coated steel plate and concrete. Over time, the airborne salt continuously penetrates and diffuses into the interior of concrete. In case PTFE separated the Al coated steel plate from concrete since airborne can't pass through the PTFE sheet, salt accumulation continuously at the edge of Al coated steel plate. Generally, the salt content at the edge is higher than that in the central area, as airborne salt from the atmospheric environment is difficult to throughout the central region by crevice. The aggressive chloride ions usually make the passive film of Al unstable and cause film breakdown and continuous pitting corrosion[41–43]. The continuous accumulation of airborne salt leads to an increase of chloride ions, which causes pitting corrosion at some

parts of the edge of Al coated steel plate. The corrosion gradually expands towards the steel substrate. In the no rain washing effect area, Al coated steel plate can contact with concrete for a long term without considering corrosion.

For areas with rain washing effect, the direct contact of Al coated steel plate and concrete, rainwater, and airborne salt throughout the crevice between Al coated steel plate and concrete. Subsequently, both chloride and rainwater can permeate into the concrete. The chloride and rainwater in the crevice will show a decreasing trend. From the results of surface and cross-sectional analysis, the corrosion behavior in this situation is not serious, the outermost Al layer remains in good condition without any corrosion observed. In the case of the PTFE group, the blocking effect of PTFE on water and chloride ions. The rainwater, and chloride ions will continue to remain between the Al coated steel plate and the PTFE sheet. This leads to relatively noticeable corrosion at the edges of Al coated steel plate. The corrosion behavior of Al coating in the PTFE case, the main corrosion behavior observed is localized pitting corrosion. The Al_2O_3 film is not stable in the solution[30,44,45]. It becomes $\text{Al}(\text{OH})_3$ by hydration, the accumulation of the hydroxide film suggested the dissolution of Al [30]. The results of XRD, aluminum hydroxide was not detected on the surface of PTFE group specimens. Under the combined effect of hydrogen evolution and attacked by the chloride ions, which breaks the passive film of Al_2O_3 into solution as AlO_2^- ions [24,30]. The breakdown of the passive state of aluminum in a chloride medium occurs through the interaction between the $\text{Al}(\text{OH})_3$ film and chloride ions, resulting in the formation of the compound AlCl_3 [46,47]. After the surface becomes saturated with corrosion products in an acidic and chloride ions-rich environment over an extended period. AlCl_3 dissolved into aluminum complex ions $[\text{AlCl}_4]^-$ become trapped in the pores of the deposits surrounding the intermetallic [30,47].

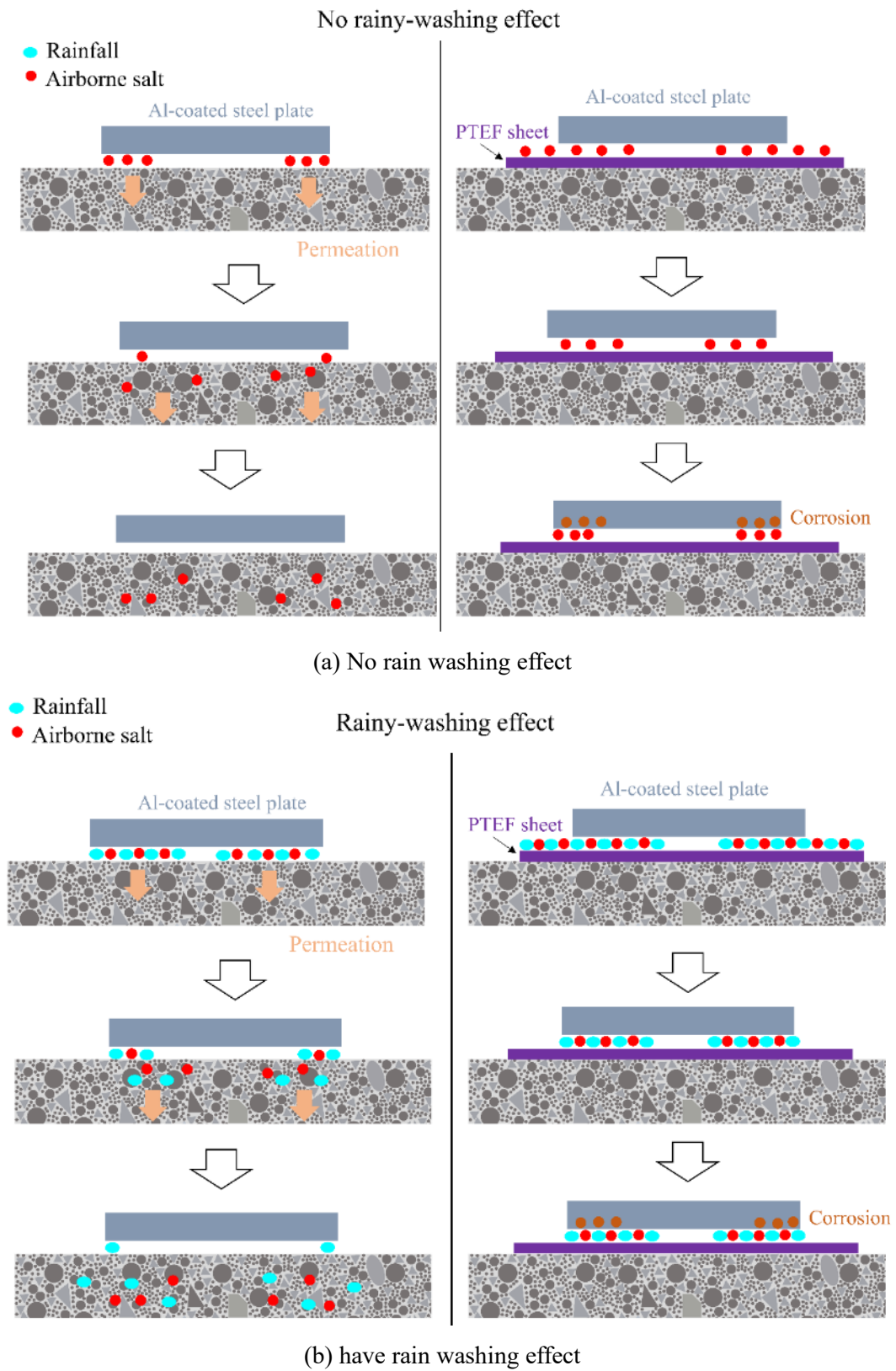


Fig. 5-11. Corrosion behavior of hot-dip Al coated steel plate contact with concrete.

5.6 Summary

In KY, there is no rain washing effect and it is very close to the sea, leading to a very large amount of salt concentration. In this case, the corrosion of the empty surface is relatively obvious, meanwhile, in the contact part no corrosion behavior can be found. This means, hot-dip Al coating contact with concrete directly in the dry environment. The concrete doesn't cause the corrosion of the Al layer. In UR and KU the condition is different from KY. Due to rain washing, the corrosion of the empty surface is relatively less, and the corrosion of the contact part is a little bit more obvious than the dry environment in KY. Due to the rain washing effect, rainwater will enter along the cracks between the Al-coated steel plate and the concrete. The stagnant water environment will cause a little corrosion behavior on the surface of the contact part. From the cross-section analysis results, although in the stagnant water environment, the corrosion behavior almost can't be found. The group of PTFE specimens is completely out of touch with concrete, comparing the corrosion behavior of contact and non-contact with concrete. The corrosion behavior of the contact case is no more serious than the PTFE case. This suggested that the corrosion behavior of Al coating contact with concrete is not serious and can be used for long-term application.

- (1) In this study, the hot-dip Al coating can be dissolved in the fresh concrete due to the highly alkaline environment. Hot-dip Al coating can't be used as a protective layer for the steel bar.
- (2) With the hardening of concrete, the pH on the concrete surface is gradually decreasing. After three days of age, the surface pH of concrete is stable. Hot-dip Al coating can contact the concrete after curing for 3 days.
- (3) In the atmospheric environment, whether there is rain washing or not. Hot-dip Al coating can contact concrete directly for long-term application.

CHAPTER 6 CONCLUSIONS AND FUTURE WORK

6.1 Main conclusions and innovations

- (1) Through the contact corrosion experiments on hot-dip aluminum, a reasonable assessment of the design combination of hot-dip aluminum on steel plates and bolts was conducted. The study involved a quantitative analysis and comparison of the extent of degradation resulting from the interaction of different metals.
- (2) Atmospheric exposure experiments of hot-dip aluminum in a marine environment were performed to predict and validate the service life of hot-dip aluminum in marine conditions.
- (3) Concrete, as one of the most common construction materials, was subjected to atmospheric exposure experiments to investigate the contact corrosion between hot-dip aluminum and dry or wet concrete. The research clarified that hot-dip aluminum can be used in contact with dry concrete.
- (4) Through experiments conducted in multiple atmospheric exposure settings, the most suitable application scenarios for hot-dip aluminum were summarized. A comparative analysis with 55Al-Zn and Zn was provided to highlight the advantages of each coating in different application scenarios.
- (5) In-depth mechanistic studies were conducted through tensile experiments to examine the mechanical properties of steel after hot-dip aluminum treatment. The research also explored the cracking and delamination processes of the coating under stress.

6.2 Summary

In this dissertation, the application of the hot-dip aluminum coating was studied. In the past many years, hot-dip galvanizing has been widely used in corrosion-resistant steel structures, but there is limited research on hot-dip aluminum. This study utilized long-term atmospheric exposure experiment data to conduct comprehensive research on the application of hot-dip aluminum in various real-world scenarios, providing recommendations for the application scenarios of hot-dip aluminum.

6.2.1 The galvanic corrosion of hot-dip Al coating applied to bolted joints

Through atmospheric exposure experiments involving the interconnection of steel structures covered by hot-dip aluminum coating and bolts made of 55Al-Zn, Zn, and stainless, atmospheric exposure test after four years of exposure evidence demonstrates that the least amount of contact corrosion issues occur when connecting hot-dip aluminum and 55Al-Zn bolts. It is recommended that hot-dip aluminum steel plates can be used in conjunction with 55Al-Zn bolt assemblies.

6.2.2 The corrosion behavior of hot-dip Al coated steel plate contact with concrete

Concrete, as one of the most widely used materials globally, encounters hot-dip aluminum, an amphoteric oxide. Hot-dip aluminum can react with both acids and bases. However, in the contact between hot-dip aluminum and damp concrete during the concrete curing process, the high pH environment can cause the hot-dip aluminum to melt. For cured concrete, the surface pH decreases, and even with long-term exposure in atmospheric exposure experiments, no contact corrosion occurs. This implies that post-cured steel structures, especially in auxiliary railings for concrete structures, can utilize hot-dip aluminum.

6.2.3 Long-term corrosion behavior of hot-dip Al coating exposure in the atmospheric environment

The research on hot-dip aluminum in a marine environment reveals its excellent corrosion resistance. Analysis of samples taken from an actual pier, constructed with steel for 25 years, shows that in locations exposed to rain, the surface aluminum layer remains intact. In areas without rain exposure, the surface aluminum layer is damaged, but the alloy layer remains sound, still providing good corrosion resistance. In urban environments, an 8-year atmospheric exposure experiment was conducted in five different exposure sites. The results indicate that, in environments with rain exposure, even in high-flying salt environments, hot-dip aluminum exhibits excellent corrosion resistance. In such conditions, the corrosion resistance of hot-dip aluminum surpasses that of 55Al-Zn and Zn. However, in environments without rain exposure, corrosion tends to occur first in the hot-dip aluminum layer, leading to comprehensive degradation of the aluminum layer. Despite this, due to the integrity of the alloy layer, it still demonstrates considerable corrosion resistance. Through studies on atmospheric exposure experiments,

the corrosion process and mechanism of hot-dip aluminum coating in the atmospheric environment have been clearly defined.

6.2.4 The mechanical properties of hot-dip Al coated steel plate

During the production process of hot-dip aluminum, the heat-affected zone generated by the metallic solution and the steel substrate leads to a decrease in the mechanical properties of the steel. Simultaneously, the mechanism the cracking and debonding process of the hot-dip aluminum coating has been elucidated.

6.3 Recommendations for the future work

This dissertation evaluated the corrosion behavior of hot-dip Al coating applied in the actual situation by the atmospheric exposure test. Explained the optimal application range and conditions for hot-dip aluminum and provided recommendations for the hot-dip materials to be used under different climatic conditions. There are still some tasks that have not been completed. In the future research, the following topics can be future investigated:

- (1) Studying the corrosion performance of hot-dip aluminum in the atmospheric environment, and the corrosion behavior of hot-dip aluminum in the soil still needs further investigation. Conducted a four-year atmospheric exposure experiment in the soil for this purpose. The experimental data is still being prepared.
- (2) Hot-dip aluminum and the alloy layer exhibit excellent corrosion resistance. In environments without rain washing, overall degradation occurs on the surface of hot-dip aluminum, but the alloy layer remains intact. An assessment of the durability of the alloy layer still requires longer-term atmospheric exposure experiments for support.
- (3) Verified through tensile experiments that the hot-dip aluminum process leads to a decrease in the mechanical performance of steel structures. The impact on large steel components can be negligible, but clearer specifications are needed for the influence on small steel structures and the usage range of hot-dip aluminum experimental bodies.

-
- (4) After the damage to the hot-dip coating, further discussion is needed on how to repair the coating, what type of coating to use for protection and the methods of repair.

REFERENCES

- [1] E.P. Najafabadi, A. Heidarpour, S. Raina, Hot-dip galvanizing of high and ultra-high strength thin-walled CHS steel tubes: Mechanical performance and coating characteristics, *Thin-Walled Struct.* 164 (2021) 107744. <https://doi.org/10.1016/j.tws.2021.107744>.
- [2] E. Kornienko, R. Ossenbrink, V. Michailov, Corrosion resistance of zinc-coated structured sheet metals, *Corros. Sci.* 69 (2013) 270–280. <https://doi.org/10.1016/j.corsci.2012.12.013>.
- [3] H. Zheng, J.G. Dai, C.S. Poon, W. Li, Influence of calcium ion in concrete pore solution on the passivation of galvanized steel bars, *Cem. Concr. Res.* 108 (2018) 46–58. <https://doi.org/10.1016/j.cemconres.2018.03.001>.
- [4] R.F. Schaller, C.F. Jove-Colon, J.M. Taylor, E.J. Schindelholz, The controlling role of sodium and carbonate on the atmospheric corrosion rate of aluminum, *Npj Mater. Degrad.* 1 (2017) 1–8. <https://doi.org/10.1038/s41529-017-0020-3>.
- [5] E. Frutos, P. Adeva, J.L. González-carrasco, P. Pérez, Surface & Coatings Technology Oxidation behavior of AISI 316 steel coated by hot dipping in an Al – Si alloy, *Surf. Coat. Technol.* 236 (2013) 188–199. <https://doi.org/10.1016/j.surfcoat.2013.09.046>.
- [6] P. Mirtaheri, S. Grimnes, Ø.G. Martinsen, Electrode polarization impedance in weak NaCl aqueous solutions, *IEEE Trans. Biomed. Eng.* 52 (2005) 2093–2099. <https://doi.org/10.1109/TBME.2005.857639>.
- [7] R.G. Du, R.G. Hu, R.S. Huang, C.J. Lin, In situ measurement of Cl⁻ concentrations and pH at the reinforcing steel/concrete interface by combination sensors, *Anal. Chem.* 78 (2006) 3179–3185. <https://doi.org/10.1021/ac0517139>.
- [8] M. Shiri, D. Rezakhani, Estimated and Stationary Atmospheric Corrosion Rate of Carbon Steel, Galvanized Steel, Copper and Aluminum in Iran, *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* 51 (2020) 342–367. <https://doi.org/10.1007/s11661-019-05509-1>.
- [9] N.C. Hosking, M.A. Ström, P.H. Shipway, C.D. Rudd, Corrosion resistance of zinc-magnesium coated steel, *Corros. Sci.* 49 (2007) 3669–3695.

-
- <https://doi.org/10.1016/j.corsci.2007.03.032>.
- [10] V. Barranco, S. Feliu, S. Feliu, EIS study of the corrosion behaviour of zinc-based coatings on steel in quiescent 3% NaCl solution. Part 1: Directly exposed coatings, *Corros. Sci.* 46 (2004) 2203–2220. <https://doi.org/10.1016/j.corsci.2003.09.032>.
- [11] A.G. Muoz, S.B. Saidman, J.B. Bessone, Corrosion of an Al-Zn-In alloy in chloride media, *Corros. Sci.* 44 (2002) 2171–2182. [https://doi.org/10.1016/S0010-938X\(02\)00042-2](https://doi.org/10.1016/S0010-938X(02)00042-2).
- [12] E. Tada, H. Kaneko, Galvanic corrosion of a Zn/steel couple in aqueous NaCl, *ISIJ Int.* 51 (2011) 1882–1889. <https://doi.org/10.2355/isijinternational.51.1882>.
- [13] K. Tachibana, Y. Morinaga, M. Mayuzumi, Hot dip fine Zn and Zn-Al alloy double coating for corrosion resistance at coastal area, *Corros. Sci.* 49 (2007) 149–157. <https://doi.org/10.1016/j.corsci.2006.05.015>.
- [14] Y.W. Liu, Z.Y. Wang, G.W. Cao, Y. Cao, Y. Huo, Study on corrosion behavior of zinc exposed in coastal-industrial atmospheric environment, *Mater. Chem. Phys.* 198 (2017) 243–249. <https://doi.org/10.1016/j.matchemphys.2017.05.043>.
- [15] T.E. Graedel, Corrosion Mechanisms for Aluminum Exposed to the Atmosphere, *J. Electrochem. Soc.* 139 (1992) 1963–1970. <https://doi.org/10.1149/1.2221162>.
- [16] A. Sehgal, Pitting in Aluminum Thin Films, *J. Electrochem. Soc.* 145 (1998) 2834. <http://jes.ecsdl.org/cgi/doi/10.1149/1.1838722>.
- [17] Z. Panossian, L. Mariaca, M. Morcillo, S. Flores, J. Rocha, J.J. Peña, F. Herrera, F. Corvo, M. Sanchez, O.T. Rincon, G. Priddybailo, J. Simancas, Steel cathodic protection afforded by zinc, aluminium and zinc/aluminium alloy coatings in the atmosphere, *Surf. Coatings Technol.* 190 (2005) 244–248. <https://doi.org/10.1016/j.surfcoat.2004.04.023>.
- [18] A.R. Moreira, Z. Panossian, P.L. Camargo, M.F. Moreira, I.C. Da Silva, J.E. Ribeiro De Carvalho, Zn/55Al coating microstructure and corrosion mechanism, *Corros. Sci.* 48 (2006) 564–576. <https://doi.org/10.1016/j.corsci.2005.02.012>.
- [19] W.J. Clark, J.D. Ramsey, R.L. McCreery, G.S. Frankel, A Galvanic Corrosion Approach to Investigating Chromate Effects on Aluminum Alloy 2024-T3, *J. Electrochem. Soc.* 149 (2002) B179. <https://doi.org/10.1149/1.1469031>.
- [20] H.C. Shih, J.W. Hsu, C.N. Sun, S.C. Chung, The lifetime assessment of hot-dip 5 %

-
- Al – Zn coatings in chloride environments, 150 (2002) 70–75.
- [21] J.L. Crolet, N. Thevenot, S. Nesic, Role of conductive corrosion products on the protectiveness of corrosion layers, NACE - Int. Corros. Conf. Ser. 1996-March (1996) 194–203.
- [22] H. Zheng, J.G. Dai, W. Li, C.S. Poon, Influence of chloride ion on depassivation of passive film on galvanized steel bars in concrete pore solution, Constr. Build. Mater. 166 (2018) 572–580. <https://doi.org/10.1016/j.conbuildmat.2018.01.174>.
- [23] V. Tavakoli Targhi, H. Omidvar, F. Sharifianjazi, A. Pakseresht, Hot corrosion behavior of aluminized and Si-modified aluminized coated IN-738LC produced by a novel hot-dip process, Surfaces and Interfaces. 21 (2020) 100599. <https://doi.org/10.1016/j.surfin.2020.100599>.
- [24] S. Li, B. Gao, S. Yin, G. Tu, G. Zhu, S. Sun, X. Zhu, The effects of RE and Si on the microstructure and corrosion resistance of Zn-6Al-3Mg hot dip coating, Appl. Surf. Sci. 357 (2015) 2004–2012. <https://doi.org/10.1016/j.apsusc.2015.09.172>.
- [25] S. Li, B. Gao, G. Tu, L. Hu, S. Sun, G. Zhu, S. Yin, Effects of magnesium on the microstructure and corrosion resistance of Zn-55Al-1.6Si coating, Constr. Build. Mater. 71 (2014) 124–131. <https://doi.org/10.1016/j.conbuildmat.2014.08.023>.
- [26] T. Pornpibunsompop, P. Thanakijkasem, Corrosion of 310S Austenitic Stainless Steel in Simulated Rocket Combustion Gas, 765 (2018) 155–159. <https://doi.org/10.4028/www.scientific.net/KEM.765.155>.
- [27] Q. Zhao, J. Zhao, X. Cheng, Y. Huang, L. Lu, X. Li, Galvanic corrosion of the anodized 7050 aluminum alloy coupled with the low hydrogen embrittlement Cd[sbnd]Ti plated 300M steel in an industrial-marine atmospheric environment, Surf. Coatings Technol. 382 (2020) 125171. <https://doi.org/10.1016/j.surfcoat.2019.125171>.
- [28] V. Kuklík, J. Kudláček, Hot-Dip galvanizing of steel structures, 2016. <https://doi.org/10.1016/C2014-0-03512-5>.
- [29] P. Pokorný, P. Tej, M. Kouřil, Evaluation of the impact of corrosion of hot-dip galvanized reinforcement on bond strength with concrete – A review, Constr. Build. Mater. 132 (2017) 271–289. <https://doi.org/10.1016/j.conbuildmat.2016.11.096>.
- [30] G. Ferraz, B. Rossi, On the fatigue behaviour of hot dip galvanized structural steel

-
- details, Eng. Fail. Anal. 118 (2020) 104834. <https://doi.org/10.1016/j.engfailanal.2020.104834>.
- [31] Y. Gao, S. Kainuma, M. Yang, S. Ishihara, D. Inoue, Galvanic corrosion behavior of hot-dip Al and 55Al–Zn coatings applied to steel bolted joints in atmospheric environments, Constr. Build. Mater. 401 (2023) 132694. <https://doi.org/10.1016/j.conbuildmat.2023.132694>.
- [32] F. García, A. Salinas, E. Nava, The role of Si and Ti additions on the formation of the alloy layer at the interface of hot-dip Al–Zn coatings on steel strips, Mater. Lett. 60 (2006) 775–778. <https://doi.org/10.1016/j.matlet.2005.10.010>.
- [33] R. Attias, B. Dlugatch, M.S. Chae, Y. Goffer, D. Aurbach, Changes in the interfacial charge-transfer resistance of Mg metal electrodes, measured by dynamic electrochemical impedance spectroscopy, Electrochem. Commun. 124 (2021) 106952. <https://doi.org/10.1016/j.elecom.2021.106952>.
- [34] Z. Eslek, A. Tulpar, Solution Preparation and Conductivity Measurements: An Experiment for Introductory Chemistry, (2013) 1665–1667.
- [35] Y. Yamada, C.H. Chiang, K. Sodeyama, J. Wang, Y. Tateyama, A. Yamada, Corrosion Prevention Mechanism of Aluminum Metal in Superconcentrated Electrolytes, ChemElectroChem. 2 (2015) 1687–1694. <https://doi.org/10.1002/celec.201500235>.
- [36] Y. Li, Corrosion behaviour of hot dip zinc and zinc-aluminium coatings on steel in seawater, Bull. Mater. Sci. 24 (2001) 355–360. <https://doi.org/10.1007/BF02708631>.
- [37] W.J. Cheng, C.J. Wang, Growth of intermetallic layer in the aluminide mild steel during hot-dipping, Surf. Coatings Technol. 204 (2009) 824–828. <https://doi.org/10.1016/j.surfcoat.2009.09.061>.
- [38] Y.H. Liu, X.Y. Chong, Y.H. Jiang, R. Zhou, J. Feng, Mechanical properties and electronic structures of Fe–Al intermetallic, Phys. B Condens. Matter. 506 (2017) 1–11. <https://doi.org/10.1016/j.physb.2016.10.032>.
- [39] J.K. Chang, C.S. Lin, W.R. Wang, S.Y. Jian, High temperature deformation behaviors of hot dip 55 wt% Al–Zn coated steel, Appl. Surf. Sci. 511 (2020) 145550. <https://doi.org/10.1016/j.apsusc.2020.145550>.

-
- [40] M. Bin Lin, C.J. Wang, Microstructure and high temperature oxidation behavior of hot-dip aluminized coating on high silicon ductile iron, *Surf. Coatings Technol.* 205 (2010) 1220–1224. <https://doi.org/10.1016/j.surfcoat.2010.08.047>.
- [41] Y. Sun, L. Wu, C. Tan, W. Zhou, B. Chen, X. Song, H. Zhao, J. Feng, Influence of Al-Si coating on microstructure and mechanical properties of fiber laser welded 22MnB5 steel, *Opt. Laser Technol.* 116 (2019) 117–127. <https://doi.org/10.1016/j.optlastec.2019.03.024>.
- [42] S. Dong, B. Zhao, C. Lin, R. Du, R. Hu, G.X. Zhang, Corrosion behavior of epoxy/zinc duplex coated rebar embedded in concrete in ocean environment, *Constr. Build. Mater.* 28 (2012) 72–78. <https://doi.org/10.1016/j.conbuildmat.2011.08.026>.
- [43] C.J. Wang, S.M. Chen, Microstructure and cyclic oxidation behavior of hot dip aluminized coating on Ni-base superalloy Inconel 718, *Surf. Coatings Technol.* 201 (2006) 3862–3866. <https://doi.org/10.1016/j.surfcoat.2006.07.242>.
- [44] K.K. Alaneme, M.O. Bodunrin, Corrosion Behavior of Alumina Reinforced Aluminium (6063) Metal Matrix Composites, *J. Miner. Mater. Charact. Eng.* 10 (2011) 1153–1165. <https://doi.org/10.4236/jmmce.2011.1012088>.
- [45] F. Yan, X. Wang, X. Wang, X. Li, C. Wang, Effect of shot peening and pre-oxidation duplex treatment on electrochemical corrosion behavior of al alloy in alkaline soil, *Int. J. Electrochem. Sci.* 12 (2017) 11212–11223. <https://doi.org/10.20964/2017.12.60>.
- [46] G. Zhong-Xiang, W. Kai, Z. Yi-Sheng, Z. Bin, Cracking and interfacial debonding of the Al-Si coating in hot stamping of pre-coated boron steel, *Appl. Surf. Sci.* 316 (2014) 595–603. <https://doi.org/10.1016/j.apsusc.2014.08.043>.
- [47] W.J. Cheng, C.J. Wang, High-temperature oxidation behavior of hot-dipped aluminide mild steel with various silicon contents, *Appl. Surf. Sci.* 274 (2013) 258–265. <https://doi.org/10.1016/j.apsusc.2013.03.030>.
- [48] A.E. Amer, M.Y. Koo, K.H. Lee, S.H. Kim, S.H. Hong, Effect of welding heat input on microstructure and mechanical properties of simulated HAZ in Cu containing microalloyed steel, *J. Mater. Sci.* 45 (2010) 1248–1254. <https://doi.org/10.1007/s10853-009-4074-7>.

-
- [49] A. Riccio, R. Ricchiuto, F. Di Caprio, A. Sellitto, A. Raimondo, Numerical investigation of constitutive material models on bonded joints in scarf repaired composite laminates, *Eng. Fract. Mech.* 173 (2017) 91–106. <https://doi.org/10.1016/j.engfracmech.2017.01.003>.
- [50] M. Shi, P. Zhang, C. Wang, F. Zhu, Effect of high heat input on toughness and microstructure of coarse grain heat affected zone in Zr bearing low carbon steel, *ISIJ Int.* 54 (2014) 932–937. <https://doi.org/10.2355/isijinternational.54.932>.
- [51] M. Yoshino, T. Tagawa, H. Li, N. Takata, Influence of Stabilizing Elements on Ductile-Brittle Transition Temperature (DBTT) of 18Cr Ferritic Stainless Steels, 62 (2022) 1–11. <https://doi.org/10.2355/isijinternational.ISIJINT-2021-506>.
- [52] L. Ceschini, A. Morri, A. Morri, G. Pivetti, Predictive equations of the tensile properties based on alloy hardness and microstructure for an A356 gravity die cast cylinder head, *Mater. Des.* 32 (2011) 1367–1375. <https://doi.org/10.1016/j.matdes.2010.09.014>.
- [53] B. Lemmens, H. Springer, M.J. Duarte, I. De Graeve, J. De Strycker, D. Raabe, K. Verbeken, Atom probe tomography of intermetallic phases and interfaces formed in dissimilar joining between Al alloys and steel, *Mater. Charact.* 120 (2016) 268–272. <https://doi.org/10.1016/j.matchar.2016.09.008>.
- [54] H. Katayama, S. Kuroda, Long-term atmospheric corrosion properties of thermally sprayed Zn, Al and Zn-Al coatings exposed in a coastal area, *Corros. Sci.* 76 (2013) 35–41. <https://doi.org/10.1016/j.corsci.2013.05.021>.
- [55] C. Wang, Y. Shen, C. Chen, M. Li, Effect of exposure to steam on corrosion of type 439 stainless steel for automotive mufflers, *J. Chinese Soc. Corros. Prot.* 36 (2016) 165–171. <https://doi.org/10.11902/1005.4537.2015.227>.
- [56] K. Hebert, R. Alkire, Growth and Passivation of Aluminum Etch Tunnels, *J. Electrochem. Soc.* 135 (1988) 2146–2157. <https://doi.org/10.1149/1.2096231>.
- [57] R. Liu, S.A. Durham, K.L. Rens, Effects of post-mercury-control fly ash on fresh and hardened concrete properties, *Constr. Build. Mater.* 25 (2011) 3283–3290. <https://doi.org/10.1016/j.conbuildmat.2011.03.016>.
- [58] Y. Gao, S. Kainuma, M. Yang, S. Ishihara, D. Inoue, Galvanic corrosion behavior of hot-dip Al and 55Al–Zn coatings applied to steel bolted joints in atmospheric

-
- environments, *Constr. Build. Mater.* 401 (2023). <https://doi.org/10.1016/j.conbuildmat.2023.132694>.
- [59] P.R. Seré, M. Zapponi, C.I. Elsner, A.R. Di Sarli, Comparative corrosion behaviour of 55Aluminium-Zinc alloy and Zinc hot-dip coatings deposited on low carbon steel substrates, *Corros. Sci.* 40 (1998) 1711–1723. [https://doi.org/10.1016/S0010-938X\(98\)00073-0](https://doi.org/10.1016/S0010-938X(98)00073-0).
- [60] A.R. Moreira, Z. Panossian, P.L. Camargo, J.E.R. De Carvalho, Zn / 55Al coating microstructure and corrosion mechanism, 48 (2006) 564–576. <https://doi.org/10.1016/j.corsci.2005.02.012>.
- [61] B. Lemmens, H. Springer, M. Peeters, I. De Graeve, J. De Strycker, D. Raabe, K. Verbeke, Deformation induced degradation of hot-dip aluminized steel, *Mater. Sci. Eng. A.* 710 (2018) 385–391. <https://doi.org/10.1016/j.msea.2017.10.094>.
- [62] H.D. Manesh, A.K. Taheri, Bond strength and formability of an aluminum-clad steel sheet, *J. Alloys Compd.* 361 (2003) 138–143. [https://doi.org/10.1016/S0925-8388\(03\)00392-X](https://doi.org/10.1016/S0925-8388(03)00392-X).
- [63] H. Bouaziz, O. Brinza, N. Haddar, M. Gasperini, M. Feki, In-situ SEM study of crack initiation, propagation and interfacial debonding of Ni-P coating during tensile tests: Heat treatment effect, *Mater. Charact.* 123 (2017) 106–114. <https://doi.org/10.1016/j.matchar.2016.11.017>.
- [64] R. Sa-nguanmoo, E. Nisaratanaporn, Y. Boonyongmaneerat, Hot-dip galvanization with pulse-electrodeposited nickel pre-coatings, *Corros. Sci.* 53 (2011) 122–126. <https://doi.org/10.1016/j.corsci.2010.09.031>.
- [65] C.A. Huang, T.H. Wang, W.C. Han, C.H. Lee, A study of the galvanic corrosion behavior of Inconel 718 after electron beam welding, *Mater. Chem. Phys.* 104 (2007) 293–300. <https://doi.org/10.1016/j.matchemphys.2007.03.017>.
- [66] G. Song, B. Johansson, S. Hapugoda, D. StJohn, Galvanic corrosion of magnesium alloy AZ91D in contact with an aluminium alloy, steel and zinc, *Corros. Sci.* 46 (2004) 955–977. [https://doi.org/10.1016/S0010-938X\(03\)00190-2](https://doi.org/10.1016/S0010-938X(03)00190-2).
- [67] M. Yoshida, S. Falco, R.I. Todd, Measurement and modelling of electrical resistivity by four-terminal method during flash sintering of 3YSZ, *J. Ceram. Soc. Japan.* 126 (2018) 579–590. <https://doi.org/10.2109/jcersj2.17256>.

-
- [68] C. Science, Electrical-resistivity Measurements of Liquid Fe–C Alloys Using the Four-terminal Method Rie ENDO,* Ryosuke IKUTA and Masahiro SUSA, 56 (2016) 2107–2109.
- [69] A.M. Simões, J.C.S. Fernandes, Studying phosphate corrosion inhibition at the cut edge of coil coated galvanized steel using the SVET and EIS, *Prog. Org. Coatings*. 69 (2010) 219–224. <https://doi.org/10.1016/j.porgcoat.2010.04.022>.
- [70] R. Pernicova, D. Dobias, P. Pokorny, Problems Connected with use of Hot-dip Galvanized Reinforcement in Concrete Elements, *Procedia Eng.* 172 (2017) 859–866. <https://doi.org/10.1016/j.proeng.2017.02.086>.
- [71] Y. Liu, Z. Wang, W. Ke, Study on influence of native oxide and corrosion products on atmospheric corrosion of pure Al, *Corros. Sci.* 80 (2014) 169–176. <https://doi.org/10.1016/j.corsci.2013.11.027>.
- [72] Y. Liu, H. Li, Z. Li, EIS investigation and structural characterization of different hot-dipped zinc-based coatings in 3.5% NaCl solution, *Int. J. Electrochem. Sci.* 8 (2013) 7753–7767.
- [73] L.F. Lima, A.L. Vieira, H. Mukai, C.M.G. Andrade, P.R.G. Fernandes, Electric impedance of aqueous KCl and NaCl solutions: Salt concentration dependence on components of the equivalent electric circuit, *J. Mol. Liq.* 241 (2017) 530–539. <https://doi.org/10.1016/j.molliq.2017.06.069>.
- [74] G. Song, S. Hapugoda, D. St John, Degradation of the surface appearance of magnesium and its alloys in simulated atmospheric environments, *Corros. Sci.* 49 (2007) 1245–1265. <https://doi.org/10.1016/j.corsci.2006.07.005>.
- [75] G. Song, A. Atrens, M. Dargusch, Influence of microstructure on the corrosion of diecast AZ91D, *Corros. Sci.* 41 (1998) 249–273. [https://doi.org/10.1016/S0010-938X\(98\)00121-8](https://doi.org/10.1016/S0010-938X(98)00121-8).
- [76] M. Yamashita, T. Nishii, H. Mizutani, Resistivity measurement by dual-configuration four-probe method, *Japanese J. Appl. Physics, Part 1 Regul. Pap. Short Notes Rev. Pap.* 42 (2003) 695–699. <https://doi.org/10.1143/jjap.42.695>.
- [77] C.S. Widodo, D.R. Santosa, U.P. Juswono, DOUBLE LAYER IMPEDANCE ANALYSIS ON THE ELECTRICAL IMPEDANCE MEASUREMENT OF SOLUTION USING A PARALLEL PLATE, 03 (2016) 65–69.

-
- [78] C.S. Widodo, H. Sela, D.R. Santosa, The effect of NaCl concentration on the ionic NaCl solutions electrical impedance value using electrochemical impedance spectroscopy methods, *AIP Conf. Proc.* 2021 (2018) 0–6. <https://doi.org/10.1063/1.5062753>.
- [79] T. Hvitved-Jacobsen, J. Vollertsen, P.H. Nielsen, A process and model concept for microbial wastewater transformations in gravity sewers, *Water Sci. Technol.* 37 (1998) 233–241. [https://doi.org/10.1016/S0273-1223\(97\)00774-9](https://doi.org/10.1016/S0273-1223(97)00774-9).
- [80] R.C. Hunt, How to increase Accuracy of solutions conductivity measurements, *Sens. Dev. Inc.* (1995) 1–17. <http://www.aitsouthwest.com/AccurateConductivity802.pdf>.
- [81] A. Nagao, F. Ishibashi, Resistivity measurement of NaCl solution by eddy-current decay method, *Jpn. J. Appl. Phys.* 15 (1976) 627–631. <https://doi.org/10.1143/JJAP.15.627>.
- [82] S.M.A. Shibli, B.N. Meena, R. Remya, A review on recent approaches in the field of hot dip zinc galvanizing process, *Surf. Coatings Technol.* 262 (2015) 210–215. <https://doi.org/10.1016/j.surfcoat.2014.12.054>.
- [83] K. Tachibana, Hot dip W ne Zn and Zn – Al alloy double coating for corrosion resistance at coastal area, 49 (2007) 149–157. <https://doi.org/10.1016/j.corsci.2006.05.015>.
- [84] M. Esmaily, N. Mortazavi, J.E. Svensson, L.G. Johansson, Evidence for an Unusual Temperature Dependence of the Atmospheric Corrosion of Zinc, *J. Electrochem. Soc.* 163 (2016) C864–C872. <https://doi.org/10.1149/2.0751614jes>.
- [85] Z. Jin, H. Chang, F. Du, T. Zhao, Y. Jiang, Y. Chen, Influence of SAP on the chloride penetration and corrosion behavior of steel bar in concrete, *Corros. Sci.* 171 (2020). <https://doi.org/10.1016/j.corsci.2020.108714>.
- [86] M. Schneider, K. Kremmer, C. Lämmel, K. Sempf, M. Herrmann, Galvanic corrosion of metal/ceramic coupling, *Corros. Sci.* 80 (2014) 191–196. <https://doi.org/10.1016/j.corsci.2013.11.024>.
- [87] K. Ghaib, F.Z. Ben-Fares, Power-to-Methane: A state-of-the-art review, *Renew. Sustain. Energy Rev.* 81 (2018) 433–446. <https://doi.org/10.1016/j.rser.2017.08.004>.

-
- [88] M.M. Mukaka, Statistics Corner: A guide to appropriate use of Correlation coefficient in medical research, *Malawi Med. J.* 24 (2012) 69–71. <https://www.ajol.info/index.php/mmj/article/view/81576>.
- [89] S. Ahmad, Reinforcement corrosion in concrete structures, its monitoring and service life prediction - A review, *Cem. Concr. Compos.* 25 (2003) 459–471. [https://doi.org/10.1016/S0958-9465\(02\)00086-0](https://doi.org/10.1016/S0958-9465(02)00086-0).
- [90] J.A. González, S. Feliú, P. Rodríguez, E. Ramírez, C. Alonso, C. Andrade, Some questions on the corrosion of steel in concrete - Part I: When, how and how much steel corrodes, *Mater. Struct. Constr.* 29 (1996) 40–46. <https://doi.org/10.1007/bf02486005>.
- [91] A. Behnood, K. Van Tittelboom, N. De Belie, Methods for measuring pH in concrete: A review, *Constr. Build. Mater.* 105 (2016) 176–188. <https://doi.org/10.1016/j.conbuildmat.2015.12.032>.
- [92] J. Elvins, J.A. Spittle, J.H. Sullivan, D.A. Worsley, The effect of magnesium additions on the microstructure and cut edge corrosion resistance of zinc aluminium alloy galvanised steel, *Corros. Sci.* 50 (2008) 1650–1658. <https://doi.org/10.1016/j.corsci.2008.02.005>.
- [93] T. Prosek, D. Thierry, C. Taxén, J. Maixner, Effect of cations on corrosion of zinc and carbon steel covered with chloride deposits under atmospheric conditions, *Corros. Sci.* 49 (2007) 2676–2693. <https://doi.org/10.1016/j.corsci.2006.11.004>.
- [94] M. Manna, G. Naidu, N. Rani, N. Bandyopadhyay, Characterisation of coating on rebar surface using Hot-dip Zn and Zn-4.9Al-0.1 misch metal bath, *Surf. Coatings Technol.* 202 (2008) 1510–1516. <https://doi.org/10.1016/j.surfcoat.2007.07.001>.
- [95] T. Gießgen, A. Mittelbach, D. Höche, M. Zheludkevich, K.U. Kainer, Enhanced predictive corrosion modeling with implicit corrosion products, *Mater. Corros.* 70 (2019) 2247–2255. <https://doi.org/10.1002/maco.201911101>.
- [96] D. YANG, J. CHEN, Q. HAN, K. LIU, Effects of lanthanum addition on corrosion resistance of hot-dipped galvalume coating, *J. Rare Earths.* 27 (2009) 114–118. [https://doi.org/10.1016/S1002-0721\(08\)60203-3](https://doi.org/10.1016/S1002-0721(08)60203-3).
- [97] Y. Wang, J. Zeng, Effects of manganese addition on microstructures and corrosion behavior of hot-dip zinc coatings of hot-rolled steels, *Surf. Coatings Technol.* 245

-
- (2014) 55–65. <https://doi.org/10.1016/j.surfcoat.2014.02.040>.
- [98] R.E. Melchers, Extreme value statistics and long-term marine pitting corrosion of steel, 23 (2008) 482–488. <https://doi.org/10.1016/j.pro bengmech.2007.09.003>.
- [99] R. Attias, B. Dlugatch, M.S. Chae, Y. Goffer, D. Aurbach, Changes in the interfacial charge-transfer resistance of Mg metal electrodes, measured by dynamic electrochemical impedance spectroscopy, *Electrochem. Commun.* 124 (2021). <https://doi.org/10.1016/j.elecom.2021.106952>.
- [100] F.J. Martin, G.T. Cheek, W.E. O’Grady, P.M. Natishan, Impedance studies of the passive film on aluminium, *Corros. Sci.* 47 (2005) 3187–3201. <https://doi.org/10.1016/j.corsci.2005.05.058>.
- [101] Z. Szklarska-Smialowska, Pitting corrosion of aluminum, *Corros. Sci.* 41 (1999) 1743–1767. [https://doi.org/10.1016/S0010-938X\(99\)00012-8](https://doi.org/10.1016/S0010-938X(99)00012-8).
- [102] A. Fabas, D. Monceau, C. Josse, P. Lamesle, Mechanism of metal dusting corrosion by pitting of a chromia-forming alloy at atmospheric pressure and low gas velocity, *Eval. Program Plann.* 107 (2016) 204–210. <https://doi.org/10.1016/j.corsci.2016.02.033>.
- [103] M. Liu, X. Cheng, X. Li, T.J. Lu, Corrosion behavior of low-Cr steel rebars in alkaline solutions with different pH in the presence of chlorides, *J. Electroanal. Chem.* 803 (2017) 40–50. <https://doi.org/10.1016/j.jelechem.2017.09.016>.
- [104] A.C. Bastos, M.G. Ferreira, A.M. Simões, Corrosion inhibition by chromate and phosphate extracts for iron substrates studied by EIS and SVET, *Corros. Sci.* 48 (2006) 1500–1512. <https://doi.org/10.1016/j.corsci.2005.05.021>.
- [105] B.O. Hasan, Galvanic corrosion of aluminum-steel under two-phase flow dispersion conditions of CO₂ gas in CaCO₃ solution, *J. Pet. Sci. Eng.* 133 (2015) 76–84. <https://doi.org/10.1016/j.petrol.2015.05.007>.
- [106] G. Vourlias, N. Pistofidis, D. Chaliampalias, E. Pavlidou, P. Patsalas, G. Stergioudis, D. Tsipas, E.K. Polychroniadis, A comparative study of the structure and the corrosion behavior of zinc coatings deposited with various methods, *Surf. Coatings Technol.* 200 (2006) 6594–6600. <https://doi.org/10.1016/j.surfcoat.2005.11.039>.
- [107] J.H. Hong, S.J. Oh, S.J. Kwon, Mössbauer analysis of the iron-zinc intermetallic

-
- phases, *Intermetallics*. 11 (2003) 207–213. [https://doi.org/10.1016/S0966-9795\(02\)00191-7](https://doi.org/10.1016/S0966-9795(02)00191-7).
- [108] T. Tamakoshi, T. Kamada, M. Shirato, Steel bridge deterioration data in Japan and modelling, *Proc. Inst. Civ. Eng. Bridg. Eng.* 170 (2017) 133–146. <https://doi.org/10.1680/jbren.16.00004>.
- [109] R. Guo, Y. Pan, L. Cai, S. Hino, Study on design formula of shear capacity of RC beams reinforced by CFRP grid with PCM shotcrete method, *Eng. Struct.* 166 (2018) 427–440. <https://doi.org/10.1016/j.engstruct.2018.03.095>.
- [110] C.T. Driscoll, W.D. Schecher, The chemistry of aluminum in the environment, *Environ. Geochem. Health*. 12 (1990) 28–49. <https://doi.org/10.1007/BF01734046>.
- [111] I. Boukerche, S. Djerad, L. Benmansour, L. Tifouti, K. Saleh, Degradability of aluminum in acidic and alkaline solutions, *Corros. Sci.* 78 (2014) 343–352. <https://doi.org/10.1016/j.corsci.2013.10.019>.
- [112] R. Parisot, S. Forest, A. Pineau, F. Grillon, X. Demonet, J.M. Mategne, Deformation and Damage Mechanisms of Zinc Coatings on Hot-Dip Galvanized Steel Sheets: Part I. Deformation Modes, *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* 35 A (2004) 797–811. <https://doi.org/10.1007/s11661-004-0007-x>.
- [113] C. Wu, W.F. Koch, K.W. Pratt, Proposed New Electrolytic Conductivity Primary Standards for KCl Solutions, 96 (1991) 191–201.
- [114] C.C. Tsaur, J.C. Rock, Y.Y. Chang, The effect of NaCl deposit and thermal cycle on an aluminide layer coated on 310 stainless steel, *Mater. Chem. Phys.* 91 (2005) 330–337. <https://doi.org/10.1016/j.matchemphys.2004.11.035>.
- [115] A. Cheng, R. Huang, J.K. Wu, C.H. Chen, Effect of rebar coating on corrosion resistance and bond strength of reinforced concrete, *Constr. Build. Mater.* 19 (2005) 404–412. <https://doi.org/10.1016/j.conbuildmat.2004.07.006>.
- [116] N. Chaubey, V.K. Singh, M.A. Quraishi, Effect of some peel extracts on the corrosion behavior of aluminum alloy in alkaline medium, *Int. J. Ind. Chem.* 6 (2015) 317–328. <https://doi.org/10.1007/s40090-015-0054-8>.
- [117] R.D. Armstrong, V.J. Braham, The mechanism of aluminium corrosion in alkaline solutions, *Corros. Sci.* 38 (1996) 1463–1471. [https://doi.org/10.1016/0010-938X\(96\)00037-6](https://doi.org/10.1016/0010-938X(96)00037-6).

-
- [118] J.B. Wang, J.M. Wang, H.B. Shao, J.Q. Zhang, C.N. Cao, The corrosion and electrochemical behaviour of pure aluminium in alkaline methanol solutions, *J. Appl. Electrochem.* 37 (2007) 753–758. <https://doi.org/10.1007/s10800-007-9310-8>.
- [119] K.C. Emregül, A.A. Aksüt, The behavior of aluminum in alkaline media, *Corros. Sci.* 42 (2000) 2051–2067. [https://doi.org/10.1016/S0010-938X\(00\)00055-X](https://doi.org/10.1016/S0010-938X(00)00055-X).
- [120] Y. Yang, H. Nakamura, T. Miura, Y. Yamamoto, Effect of corrosion-induced crack and corroded rebar shape on bond behavior, *Struct. Concr.* 20 (2019) 2171–2182. <https://doi.org/10.1002/suco.201800313>.
- [121] A.C. Bastos, M.C. Quevedo, M.G.S. Ferreira, The influence of vibration and probe movement on SVET measurements, *Corros. Sci.* 92 (2015) 309–314. <https://doi.org/10.1016/j.corsci.2014.10.038>.
- [122] R. Hausbrand, M. Stratmann, M. Rohwerder, Corrosion of zinc-magnesium coatings: Mechanism of paint delamination, *Corros. Sci.* 51 (2009) 2107–2114. <https://doi.org/10.1016/j.corsci.2009.05.042>.
- [123] N.M. Nor, A. Haddad, H. Griffiths, Performance of earthing systems of low resistivity soils, *IEEE Trans. Power Deliv.* 21 (2006) 2039–2047. <https://doi.org/10.1109/TPWRD.2006.874656>.
- [124] R. Vicentini, L.M. Da Silva, E.P. Cecilio, T.A. Alves, W.G. Nunes, H. Zanin, How to measure and calculate equivalent series resistance of electric double-layer capacitors, *Molecules.* 24 (2019). <https://doi.org/10.3390/molecules24081452>.
- [125] D.A. Wadeson, X. Zhou, G.E. Thompson, P. Skeldon, L.D. Oosterkamp, G. Scamans, Corrosion behaviour of friction stir welded AA7108 T79 aluminium alloy, *Corros. Sci.* 48 (2006) 887–897. <https://doi.org/10.1016/j.corsci.2005.02.020>.
- [126] S. Kainuma, M. Yang, Y. Gao, M. Hashimoto, Long-term deterioration mechanism of hot-dip aluminum coating exposed to a coastal-atmospheric environment, *Constr. Build. Mater.* 280 (2021) 122516. <https://doi.org/10.1016/j.conbuildmat.2021.122516>.
- [127] ASTM A53/A53M – 12, Standard Specification for Pipe, Steel, Black and Hot-Dipped, Zinc-Coated, Welded and Seamless, Am. Soc. Test. Mater. Int. West

-
- Conshohocken, PA, Wwww.Astm.Org. (2001) 5–8. <https://doi.org/10.1520/A0053>.
- [128] D. Mizuno, S. Suzuki, S. Fujita, N. Hara, Corrosion monitoring and materials selection for automotive environments by using Atmospheric Corrosion Monitor (ACM) sensor, *Corros. Sci.* 83 (2014) 217–225. <https://doi.org/10.1016/j.corsci.2014.02.020>.
- [129] G. Priyotomo, S. Prifiarni, L. Nuraini, J. Triwardono, A. Royani, Sundjono, I. Purawiardi, H. Gunawan, A field study of atmospheric corrosion of carbon steel after short exposure in pelabuhan ratu, west java province, indonesia, *Walailak J. Sci. Technol.* 18 (2021). <https://doi.org/10.48048/wjst.2021.9667>.
- [130] N.S. Palsson, K. Wongpinkaw, P. Khamsuk, S. Sorachot, W. Pongsaksawad, Outdoor atmospheric corrosion of carbon steel and weathering steel exposed to the tropical-coastal climate of Thailand, *Mater. Corros.* 71 (2020) 1019–1034. <https://doi.org/10.1002/maco.201911340>.
- [131] J. Alcántara, B. Chico, I. Díaz, D. de la Fuente, M. Morcillo, Airborne chloride deposit and its effect on marine atmospheric corrosion of mild steel, *Corros. Sci.* 97 (2015) 74–88. <https://doi.org/10.1016/j.corsci.2015.04.015>.
- [132] J. Wang, Q. Huang, J. Liu, Y. Zhang, C. Qiao, L. Hao, J. Dong, W. Ke, Accelerated Indoor Corrosion of Galvanized Steel in a Simulated Atmospheric Environment of Guangzhou Area, *Cailiao Yanjiu Xuebao/Chinese J. Mater. Res.* 32 (2018) 631–640. <https://doi.org/10.11901/1005.3093.2017.543>.
- [133] N. Birbilis, R.G. Buchheit, Investigation and Discussion of Characteristics for Intermetallic Phases Common to Aluminum Alloys as a Function of Solution pH, *J. Electrochem. Soc.* 155 (2008) C117. <https://doi.org/10.1149/1.2829897>.
- [134] Y. Yu, Y. Zuo, Z. Zhang, L. Wu, C. Ning, C. Zuo, Al₂O₃ coatings on zinc for anti-corrosion in alkaline solution by electrospinning, *Coatings.* 9 (2019). <https://doi.org/10.3390/coatings9110692>.
- [135] H. Ezuber, Materials & Design A study on the corrosion behavior of aluminum alloys in seawater, 29 (2008) 801–805. <https://doi.org/10.1016/j.matdes.2007.01.021>.
- [136] M. Ozawa, S. Uchida, T. Kamada, H. Morimoto, Study of mechanisms of explosive spalling in high-strength concrete at high temperatures using acoustic

-
- emission, *Constr. Build. Mater.* 37 (2012) 621–628. <https://doi.org/10.1016/j.conbuildmat.2012.06.070>.
- [137] E. Sistonen, A. Cwirzen, J. Puttonen, Corrosion mechanism of hot-dip galvanised reinforcement bar in cracked concrete, *Corros. Sci.* 50 (2008) 3416–3428. <https://doi.org/10.1016/j.corsci.2008.08.050>.
- [138] P.K. Sharma, V. V. Varadan, V.K. Varadan, A critical role of pH in the colloidal synthesis and phase transformation of nano size α -Al₂O₃ with high surface area, *J. Eur. Ceram. Soc.* 23 (2003) 659–666. [https://doi.org/10.1016/S0955-2219\(02\)00191-7](https://doi.org/10.1016/S0955-2219(02)00191-7).
- [139] E.T.H. Hiinggerberg, Micro- and nanotechniques to study localized corrosion, 40 (1995) 1361–1368. [https://doi.org/10.1016/0013-4686\(95\)00072-M](https://doi.org/10.1016/0013-4686(95)00072-M).
- [140] Y. Xu, M. Yongjun, Probing the initiation and propagation processes of flow accelerated corrosion and erosion corrosion under simulated turbulent flow conditions, *Corros. Sci.* 151 (2019) 163–174. <https://doi.org/10.1016/j.corsci.2019.01.028>.
- [141] M. Luria, R.E. Imhoff, R.J. Valente, W.J. Parkhurst, R.L. Tanner, Rates of conversion of sulfur dioxide to sulfate in a scrubbed power plant plume, *J. Air Waste Manag. Assoc.* 51 (2001) 1408–1413. <https://doi.org/10.1080/10473289.2001.10464368>.
- [142] S. Okabe, M. Odagiri, T. Ito, H. Satoh, Succession of sulfur-oxidizing bacteria in the microbial community on corroding concrete in sewer systems, *Appl. Environ. Microbiol.* 73 (2007) 971–980. <https://doi.org/10.1128/AEM.02054-06>.
- [143] W.X. Wang, Y. Takao, T. Matsubara, C. Uchimura, S. Baba, M. Higashijima, Development of galvanic corrosion-resistant CFML based on composite coating, *Zair. Soc. Mater. Sci. Japan.* 56 (2007) 420–425. <https://doi.org/10.2472/jsms.56.420>.
- [144] B. Elsener, Macrocell corrosion of steel in concrete - Implications for corrosion monitoring, *Cem. Concr. Compos.* 24 (2002) 65–72. [https://doi.org/10.1016/S0958-9465\(01\)00027-0](https://doi.org/10.1016/S0958-9465(01)00027-0).
- [145] A.M. Simões, A.C. Bastos, M.G. Ferreira, Y. González-García, S. González, R.M. Souto, Use of SVET and SECM to study the galvanic corrosion of an iron-zinc cell,

-
- Corros. Sci. 49 (2007) 726–739. <https://doi.org/10.1016/j.corsci.2006.04.021>.
- [146] S. Kainuma, Y.S. Jeong, J.H. Ahn, Investigation on the stress concentration effect at the corroded surface achieved by atmospheric exposure test, Mater. Sci. Eng. A. 602 (2014) 89–97. <https://doi.org/10.1016/j.msea.2014.02.056>.
- [147] A. Rajabipour, R.E. Melchers, A numerical study of damage caused by combined pitting corrosion and axial stress in steel pipes, Corros. Sci. 76 (2013) 292–301. <https://doi.org/10.1016/j.corsci.2013.07.002>.
- [148] T.U. Mohammed, H. Hamada, H. Yokota, Macro- And micro-cell corrosion of steel bars in cracked concrete made with various cements, Am. Concr. Institute, ACI Spec. Publ. SP-221 (2004) 51–72. <https://doi.org/10.14359/13246>.
- [149] T. Nakai, H. Matsushita, N. Yamamoto, Effect of pitting corrosion on local strength of hold frames of bulk carriers (2nd Report) - Lateral-distortional buckling and local face buckling, Mar. Struct. 17 (2004) 612–641. <https://doi.org/10.1016/j.marstruc.2005.03.001>.
- [150] R.E. Melchers, The effect of corrosion on the structural reliability of steel offshore structures, Corros. Sci. 47 (2005) 2391–2410. <https://doi.org/10.1016/j.corsci.2005.04.004>.
- [151] D. Ouinas, B. Bachir Bouiadjra, B. Achour, N. Benderdouche, Modelling of a cracked aluminium plate repaired with composite octagonal patch in mode I and mixed mode, Mater. Des. 30 (2009) 590–595. <https://doi.org/10.1016/j.matdes.2008.05.040>.
- [152] M.Z. Yang, M. Wilmott, J.L. Luo, Crevice corrosion behavior of A516-70 carbon steel in solutions containing inhibitors and chloride ions, Thin Solid Films. 326 (1998) 180–188. [https://doi.org/10.1016/S0040-6090\(98\)00517-3](https://doi.org/10.1016/S0040-6090(98)00517-3).
- [153] C. Liu, R.I. Revilla, D. Zhang, Z. Liu, A. Lutz, F. Zhang, T. Zhao, H. Ma, X. Li, H. Terryn, Role of Al₂O₃ inclusions on the localized corrosion of Q460NH weathering steel in marine environment, Corros. Sci. 138 (2018) 96–104. <https://doi.org/10.1016/j.corsci.2018.04.007>.
- [154] S. Schürz, G.H. Luckeneder, M. Fleischanderl, P. Mack, H. Gsaller, A.C. Kneissl, G. Mori, Chemistry of corrosion products on Zn-Al-Mg alloy coated steel, Corros. Sci. 52 (2010) 3271–3279. <https://doi.org/10.1016/j.corsci.2010.05.044>.

-
- [155] F. Ahmed, K. Durst, S. Rosiwal, J. Fandrey, J. Schaufler, M. Göken, In-situ tensile testing of crystalline diamond coatings using Raman spectroscopy, *Surf. Coatings Technol.* 204 (2009) 1022–1025. <https://doi.org/10.1016/j.surfcoat.2009.04.030>.
- [156] G.H. Awan, F. ul Hasan, The morphology of coating/substrate interface in hot-dip-aluminized steels, *Mater. Sci. Eng. A.* 472 (2008) 157–165. <https://doi.org/10.1016/j.msea.2007.03.013>.
- [157] J. Chen, Y. Song, D. Shan, E.H. Han, Study of the corrosion mechanism of the in situ grown Mg-Al-CO 32- hydrotalcite film on AZ31 alloy, *Corros. Sci.* 65 (2012) 268–277. <https://doi.org/10.1016/j.corsci.2012.08.026>.
- [158] L. Kang, H. Ge, T. Kato, Experimental and ductile fracture model study of single-groove welded joints under monotonic loading, *Eng. Struct.* 85 (2015) 36–51. <https://doi.org/10.1016/j.engstruct.2014.12.006>.
- [159] S.M. Manhabosco, R.J.C. Batista, S.N. Da Silva, L.F.P. Dick, Determination of current maps by svet of hot-dip galvanized steel under simultaneous straining, *Electrochim. Acta.* 168 (2015) 89–96. <https://doi.org/10.1016/j.electacta.2015.03.162>.
- [160] J. Inoue, S. Nambu, Y. Ishimoto, T. Koseki, Fracture elongation of brittle/ductile multilayered steel composites with a strong interface, *Scr. Mater.* 59 (2008) 1055–1058. <https://doi.org/10.1016/j.scriptamat.2008.07.020>.
- [161] S. Halder, D. Basu, Response of Euler-Bernoulli beam on spatially random elastic soil, *Comput. Geotech.* 50 (2013) 110–128. <https://doi.org/10.1016/j.compgeo.2013.01.002>.
- [162] A.A. Moya, Electrochemical Impedance of Ion-Exchange Membranes with Interfacial Charge Transfer Resistances, *J. Phys. Chem. C.* 120 (2016) 6543–6552. <https://doi.org/10.1021/acs.jpcc.5b12087>.
- [163] C. Xie, W. Tong, Cracking and decohesion of a thin Al₂O₃ film on a ductile Al-5%Mg substrate, *Acta Mater.* 53 (2005) 477–485. <https://doi.org/10.1016/j.actamat.2004.10.005>.
- [164] V. Krivy, M. Kubzova, K. Kreislova, V. Urban, Characterization of corrosion products on weathering steel bridges influenced by chloride deposition, *Metals (Basel)*. 7 (2017). <https://doi.org/10.3390/met7090336>.

-
- [165] H.C. Lee, J. man Choi, B. Lee, T.G. Kim, Failure analysis of stress corrosion cracking in aircraft bolts, *Eng. Fail. Anal.* 14 (2007) 209–217. <https://doi.org/10.1016/j.engfailanal.2005.10.021>.
- [166] F. Delannay, P. Warren, On crack interaction and crack density in strain-induced cracking of brittle films on ductile substrates, *Acta Metall. Mater.* 39 (1991) 1061–1072. [https://doi.org/10.1016/0956-7151\(91\)90193-5](https://doi.org/10.1016/0956-7151(91)90193-5).
- [167] W.J. Yi, Y. Zhou, H.J. Hwang, Z.J. Cheng, X. Hu, Cyclic loading test for circular reinforced concrete columns subjected to near-fault ground motion, *Soil Dyn. Earthq. Eng.* 112 (2018) 8–17. <https://doi.org/10.1016/j.soildyn.2018.04.026>.
- [168] S. Krishnamurthy, I. Reimanis, Multiple cracking in CrN and Cr2N films on brass, *Surf. Coatings Technol.* 192 (2005) 291–298. <https://doi.org/10.1016/j.surfcoat.2004.06.025>.

ACKNOWLEDGEMENT

Foremost, I would like to express my deepest appreciation to my supervisor, Prof. Shigenobu Kainuma, whose expertise was invaluable in formulating the research and methodology. His guidance helped me in all the time of research and writing this dissertation.

Besides my supervisor, I would like to thank the dissertation examining committee: Prof. Chihiro Morita and Prof. Hiroaki Nakano. Your insightful feedback pushed me to sharpen my thinking and brought my work to a higher level.

I would like to acknowledge Dr. Shuji Ishihara from the Research & Development Center, Mitsui E & S Machinery Co., Ltd. Your extensive experience in applied research has been immensely helpful to me, and your profound knowledge and rich research background are truly valuable. My sincerest thanks to Mr. Daichi Inoue and Mr. Ryuichi Minada for every discussion and great support behind our collaborative research. Your contributions have been instrumental in the smooth progress of our research. I would particularly like to single out Research Associate Professor Muye Yang, I appreciate your guidance and helpful advice since my master's program, which has been invaluable to me in my research endeavors. If it weren't for your patient guidance, I wouldn't entered the doctoral program. In addition, I would like to express my gratitude to Research Assistant Professor Aran Kim, thank you for your assistance in both my research and life. Your optimism and cheerfulness have profoundly influenced me. Also express thanks to Secretary Ms. Reiko Kato and Ms. Sayuri Gondo, Technical staff Mr. Hiroyuki Shibata in the structural design laboratory, for their patient support.

My sincere thanks also go to fellow labmates: Kosuke Yagi, Shusen Zhuang, Angzhi Hasegawa, Kazuya Yamashita, Sanghong Park, Lianheng Cai, Jian Tang, Jie Xu, Weikun Xu, Haoxuan Yang, Jiajing Xie, Maoling Zhao, Saki Okada, Shengyue Li, Juejiang Yu, Yingrui Ju, Keisuke Suzuki, Ryohei Toyota, and Kaishi Takaki, for the stimulating discussions, for the sleepless nights we were working together, and for all the fun we have had.

Last but not least, I would like to thank my family, for supporting me throughout my life. At the end of this article, I would like to express my gratitude separately to my mother.

Although I can no longer share any joys or sorrows with you, and you can only appear in my memory, I am very thankful for teaching me not to give up in the face of difficulties. If it weren't for the commitment, I made to you like a sealed promise, there were several times during this process when I wanted to give up. I will continue my future life with your optimism and kindness.

APPENDIX

CHAPTER 7 MECHANICAL PROPERTIES OF HOT-DIP COATED STEEL PLATE

7.1 Introduction

Hot-dip aluminum coating on low-carbon steel has found widespread application in boilers and exhaust pipes in high-temperature environments due to the formation of fine and dense Al_2O_3 oxide on the steel surface. When steel is used in high-temperature environments, this provides excellent oxidation resistance [43,153]. The microstructure of the hot-dip aluminum protective coating on steel is composed of an intermetallic layer of Fe-Al alloy formed by the mutual diffusion of Fe and Al during the hot-dip process, which is different from the aluminum surface coating with the same composition as the aluminum bath. The metal interlayer in hot-dip low-carbon steel consists of secondary FeAl_3 and primary Fe_2Al_5 , with irregular interfaces between the Fe-Al interlayer and the steel substrate, which is referred to as a tongue-like morphology. This irregular interface may not be conducive to the wear resistance and thermal stability of the aluminum layer, as it can lead to stress concentrations within the aluminum layer, causing cracking during assembly or at high temperatures. Various studies have proposed different hypotheses regarding the growth mechanism of the tongue-like morphology in aluminum-treated low-carbon steel [154].

Research by Kwon and Rahmel suggests that the tongue-like morphology is related to the grain boundaries and grain size of the steel substrate [40,107]. On the other hand, numerous studies indicate that Fe_2Al_5 preferentially grows along specific diffusion directions, implying that the anisotropic growth of Fe_2Al_5 results in the tongue-like morphology [155–157]. Due to the mutual diffusion of Fe and Al and the presence of interlayer tongue-like structures, the thickness of the aluminum layer gradually increases with extended immersion time, making the distinction between the interlayer and the steel substrate more pronounced. Consequently, the evolution of the interlayer structure not only affects the mechanical properties of aluminum-treated steel but also influences its durability. To understand the growth mechanism of the interlayer, the microstructure and

phase composition evolution of the metal interlayer in hot-dip low-carbon steel after different immersion times were investigated.

7.2 Experimental

The specimens are made from carbon steel plates (JIS G 3106 SM490A) with two different plate thickness t : 9 and 12 mm. The types of tensile specimens are shown in Table 7-1. There are four groups of specimens, 1) without coating, 2) specimen coated by hot-dip Al coating, 3) coated by hot-dip 55Al-Zn coating 4) coated by hot-dip Zn coating. The dimensions of the specimen are specified in JIS Z2241-1A, the detailed configuration is shown in Fig. 7-1. Moreover, all specimens were tested by the MTS machine, under displacement control and the tensile speed was 0.03 mm/sec. A specimen under the loading is shown in Fig. 7-2. During the test process, load P and displacement δ were measured and recorded by a data logger. Furthermore, the surface crack initiation behaviors of all specimens were recorded continuously by a camera. The hardness of the cross-section in the tensile test was obtained by the microhardness tester (HMV-G30S, SHIMADZU Corporation). The hardness was measured every 15 μ m from the top of the cross-section surface. The SEM image of the fracture surface was gained by the scanning electron microscope using the SE model (SU3500 HITACHI Inc.).

Tensile test was not only used to evaluate the coating fracture stress and interfacial strength between the coating and substrate, but also estimate the heat effect on the mechanical properties of steel substrates during the coating process. All specimens were subject to 2000kN universal tension machine under the displacement control. During the test, load P and the point displacement were measured by the data logger. Tensile speed is 0.014mm/s. In order to study the cracking and interfacial debonding condition of specimens, the specimen was fixed into the epoxy resin after the tensile test. The specimen was cut along the loading direction. The surface of the cross section was polished by the

Table 7-1. Types of specimens in tensile test.

Type	Coating condition	Molten metal temperature (°C)	Specimen thickness t (mm)
N	Without coating	-	9, 12
Al	Al coating	700–750 °C	
55Al-Zn	55Al-Zn coating	595–610 °C	
Zn	Zn coating	440–460 °C	

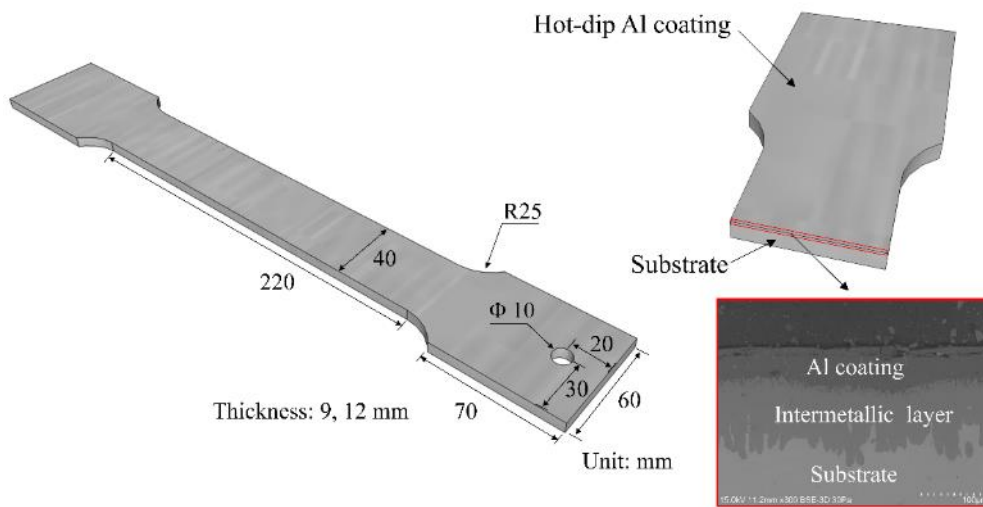


Fig. 7-1. Schematic diagram of the specimens in the tensile test.

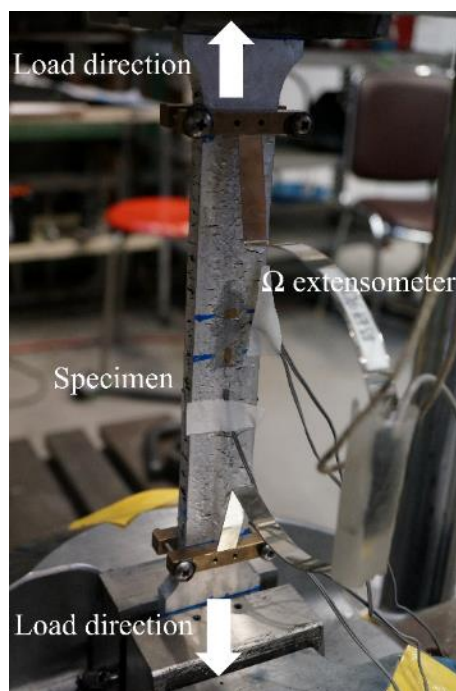


Fig. 7-2 Photograph of specimen in tensile test.

sandpaper from #400 to #2000. The cross section along the loading direction was observed by the optical microscope. The fracture surface was observed by the scanning

electron microscope. (SU3500 HITACHI)

7.3 Tensile test results

The detachment and peeling of the metal coating after the hot-dip aluminum tensile test are shown in Fig. 7-3. Through observation, it is found that the interfacial delamination of hot-dip aluminum is the most pronounced, while the peeling condition of hot-dip Zn is the least apparent. By analyzing the cross-section of the hot-dip, it can be observed that the morphology of the metal hot-dip cross-section is divided into three layers. The outermost layer has the same composition as the plating solution. Due to the high temperature of the plating solution, there is an alloy layer between the outermost layer and the steel base, which is formed by the mutual fusion and diffusion of the steel base and the plating solution during the hot-dip process. The tensile test explains, from a mechanical perspective, the influence of thermal effects on the material's mechanical properties during the hot-dip process. It also provides an in-depth exploration of the changes and mechanisms of the coating during the tensile process. The load and displacement curve illustrates the relationship between the load applied to the material during the test and the displacement. The shape and features of this curve provide crucial information about the material's performance and behavior. The load-displacement curve can describe the mechanical properties of the material during elastic, plastic, and fracture processes. The load is depicted on the curve as shown in Fig. 7-4, indicating excellent repeatability and stable experimental data.

From the test data, it can be observed that for isotropic materials like steel and metal, mechanical properties are highly stable. The experimental data for the same type of specimen show very little variation each time. The load-displacement curves for the tensile specimens of hot-dip aluminum, 55Al-Zn, and Zn, compared with the uncoated specimens, are presented in Fig. 7-5. Through the comparison, it is found that the curve for the hot-dip Zn specimen closely aligns with the uncoated specimen. This can be understood as the minimal thermal impact of hot-dip Zn on steel, as indeed, the temperature during the hot-dip Zn process is the lowest among all experimental conditions, and this temperature does not significantly affect the mechanical properties of

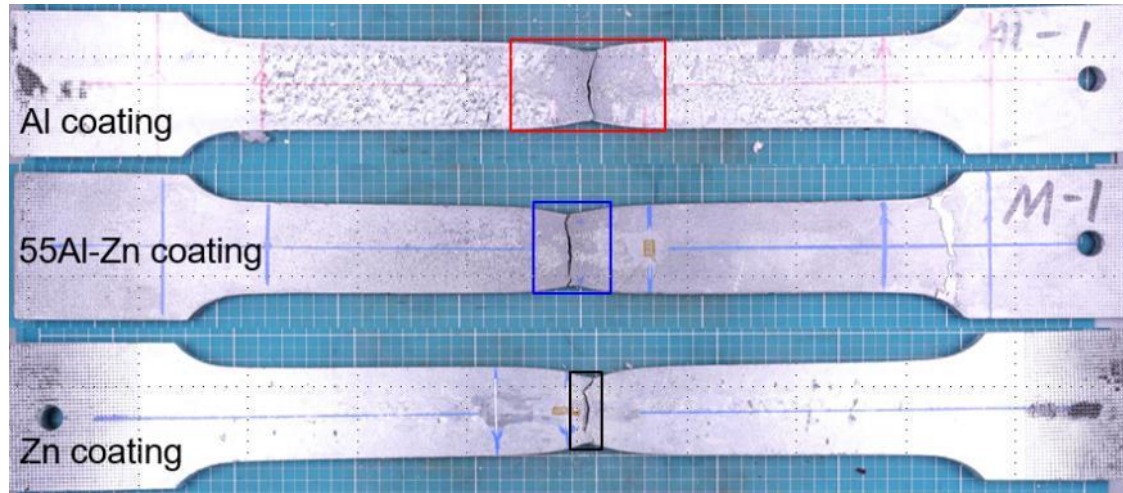
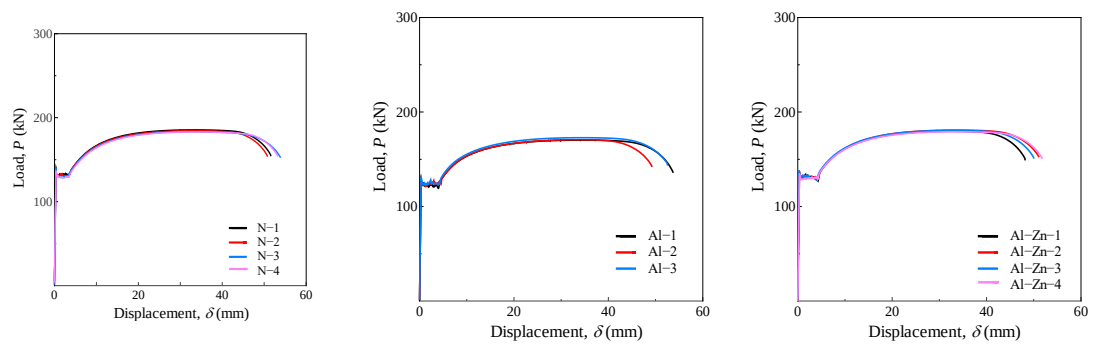
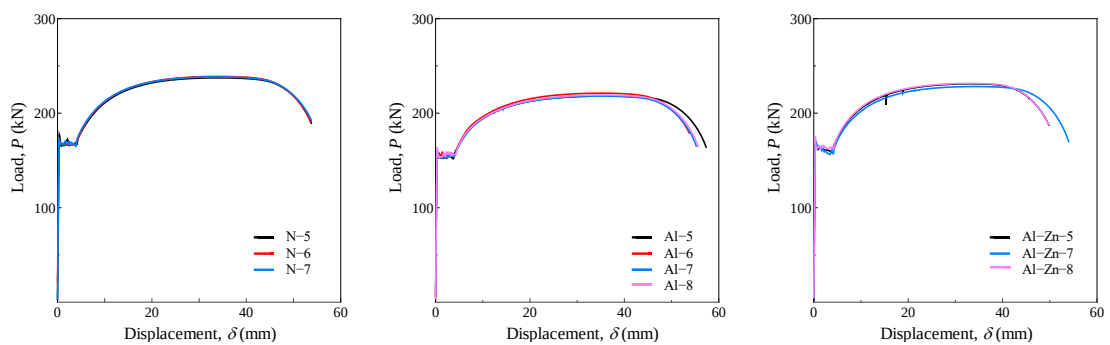


Fig. 7-3 The cracking and debonding of coatings after tensile test.



(a) Plate thickness $t=9$ mm



(b) Plate thickness $t=12$ mm

Fig. 7-4 Load and displacement curves

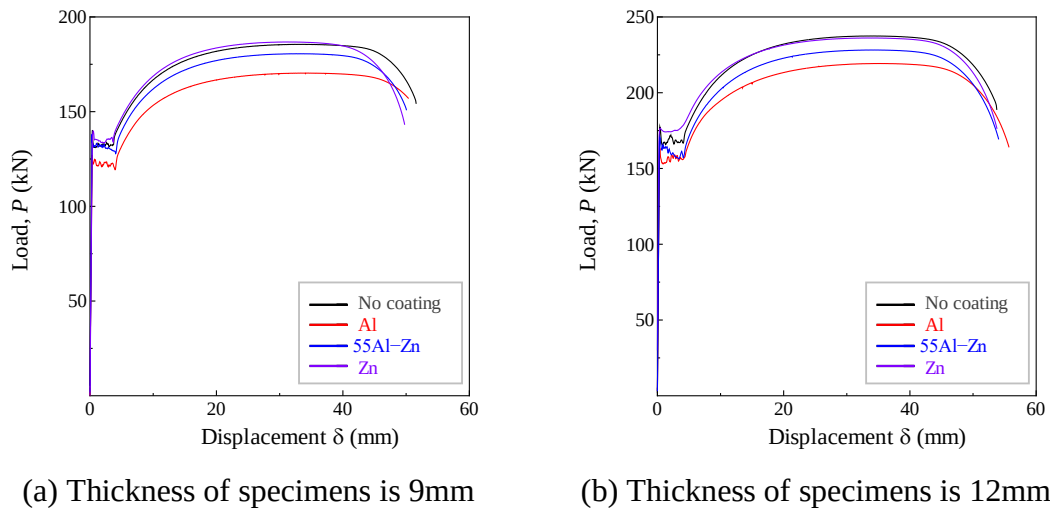


Fig. 7-5 Load and displacement curves of three kinds of hot-dip coatings.

steel. From the load-displacement curves, certain phenomena can also be observed, both in the 9mm and 12mm tensile experiments. It can be seen that the tensile strength and yield strength of the hot-dip aluminum specimen are lower than those of the uncoated specimen. The tensile strength and yield strength of the hot-dip 55Al-Zn specimen falls between those of the hot-dip aluminum specimen and the uncoated specimen. This sequence is consistent with the order of the melting baths for these three hot-dip metals. In the molten metal bath, the temperature is highest for hot-dip aluminum and lowest for hot-dip Zn. The degradation of material mechanical properties also supports the same conclusion. Due to the influence of temperature, hot-dip aluminum has the most significant impact on the mechanical properties of steel. A quantitative analysis of specific numerical values will be conducted in subsequent research. Comparing the four $P-\delta$ curves, only the mechanical properties of the specimen coated by Al coating decrease can be found obviously. The decreasing yield limit and the maximum load limit can be easily detected. The detailed mechanical parameters (tensile strength, yield strength, elongation) are shown in Fig. 7-6. No coating specimen was set as a standard, the other specimens are the relative percentages to no coating specimens. The tensile strength and yield strength of the Al-coated specimen have a decreasing trend compared with no coating specimen. The other types specimens, although there also have a decreased trend, the decline is not obvious. The effect of the thickness of the specimens on the elongation is more obvious. For the 12mm thickness specimens, the elongation of hot-dip coating coated specimens is similar to no coating specimen. For the 9mm specimens,

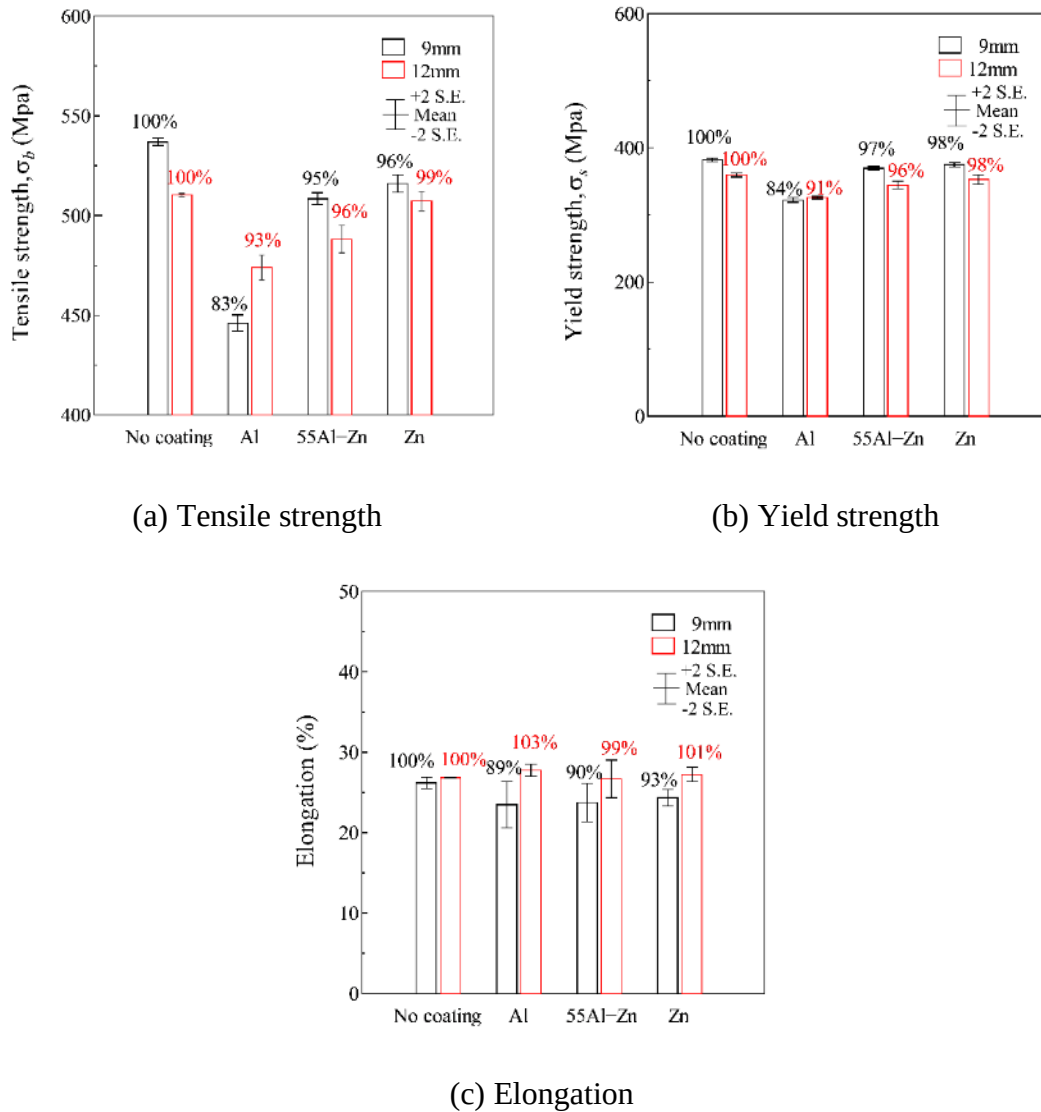


Fig. 7-6 The mechanical properties of hot-dip coatings in tensile test.

the elongation of coated specimens decreased but the decline is also not obvious. The main factor affecting the elongation is the thickness of the specimens. To study the reason for the decreasing mechanical properties of the Al coated specimen, the hardness measurement was carried out on the cross-section of tensile specimen. The hardness of the Al coating layer, intermetallic layer, HAZ and substrate can be easily distinguished. The intermetallic layer formed due to the fusion of molten Al and iron at a temperature over 700 °C. This layer consists of the FeAl_3 and Fe_2Al_5 and has a higher hardness. The center part of the fracture surface is the typical ductile fracture. The edge of the fracture

surface is the junction of the intermetallic layer and steel substrate. After the tensile test, the outermost Al layer cracked and showed interfacial debonding behavior. Therefore, the Al layer can't be found on the fracture surface. The fracture behavior of the edge part is different from the center part, the main fracture model is a brittle fracture that is detected from the SEM image. The fracture surface of the brittle is relatively flat, the microstructure is similar to a dimple that can't be found. The tensile strength of brittle materials is generally poor. In addition, the microstructure of HAZ consisted of acicular ferrite and grain boundary ferrite at prior austenite grain boundaries. The Austenite grain size of HAZ increases with heat input increasing due to long holding time at peak temperature. The Vickers hardness of HAZ was decreased with the increase of heat input. The hardness has a positive correlation with the tensile properties of the steel substrate. The hardness of hot-dip aluminum coating from the surface to the steel substrate in the vertical direction is shown in Fig. 7-7. Due to the exceptionally high hardness of the Fe-Al alloy region, the material of Fe-Al, being a brittle material, is prone to brittle fracture under tensile stress in the tensile test. When subjected to external loads, it lacks sufficient resistance. A noticeable decrease in hardness is observed in the steel substrate at the interface with Fe-Al. For materials composed of a steel substrate, hardness can to some extent represent the tensile properties of the material, and a decrease in hardness leads to a decline in the material's tensile performance. It indicated that the tensile properties

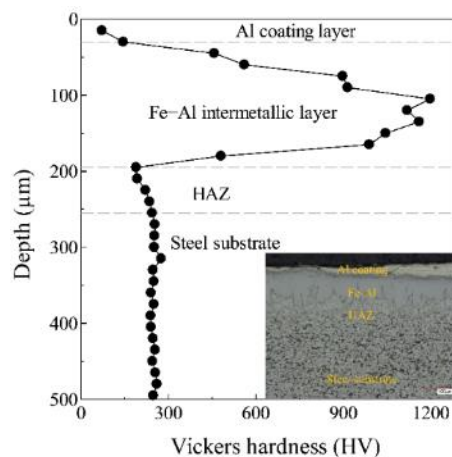


Fig. 7-7 The hardness test of hot-dip Al coating tensile test.

decreased in the HAZ. The mechanical properties decreasing of hot-dip Al coated specimen was composed of two reasons. One is the brittle fracture of the intermetallic layer and the other is the mechanical properties decreasing behavior in the HAZ.

7.4 Fractography and fracture mechanism of specimens

After completing the tensile test of hot-dip aluminum, a phase observation of the cross-section of the tensile specimen was carried out. In order to clearly observe the microfeatures and undulations of the cross-section, the SEM's SE mode was selected for microscopic observation. The fracture surfaces of ductile and brittle fractures exhibit completely different morphological features. For the ductile fracture, the tensile region undergoes significant plastic deformation and necking, resulting in local contraction. This leads to a cup-shaped or conical fracture surface. During ductile tensile deformation, microscopic cracks gradually merge into larger cracks, ultimately causing fracture. The characteristics of brittle fractures are entirely different from ductile fractures. The fracture surface appears relatively flat, with almost no noticeable necking or tensile region. Brittle fractures typically occur without significant plastic deformation, resulting in a relatively flat fracture surface. Microscopic observations of the tensile test fracture surface are

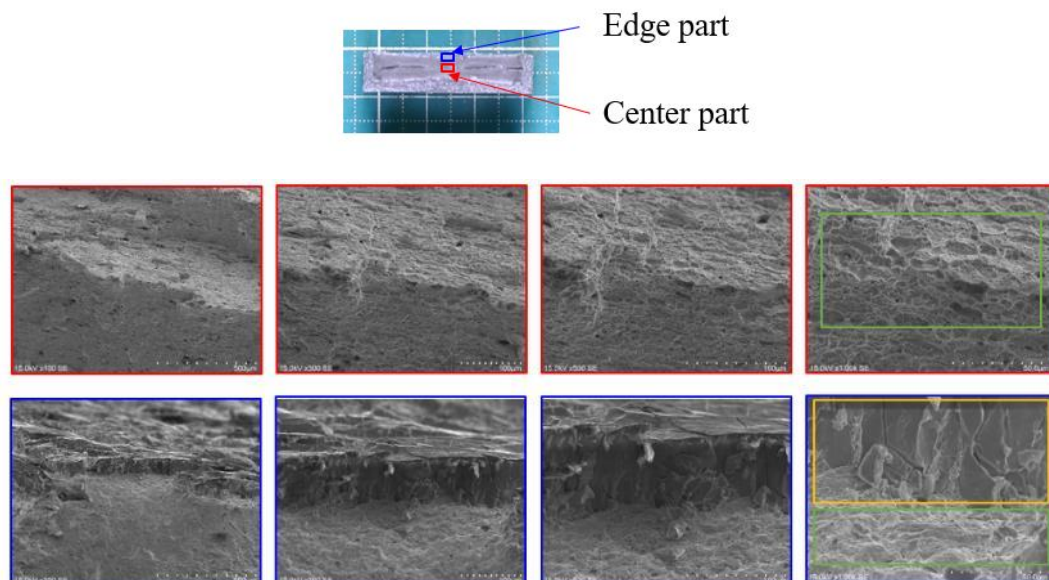


Fig. 7-8 The fracture surface microstructure of the hot-dip Al coating specimen.

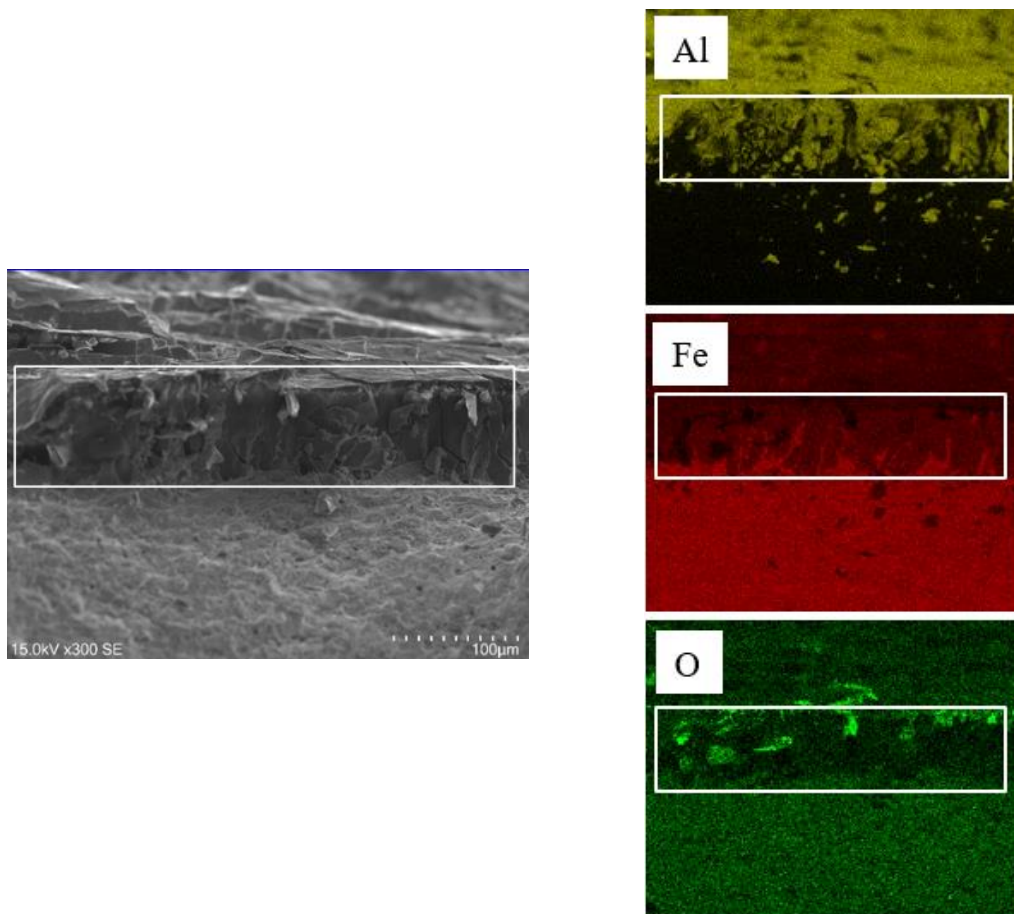


Fig. 7-9 The SEM-EDS analysis of the brittle fracture.

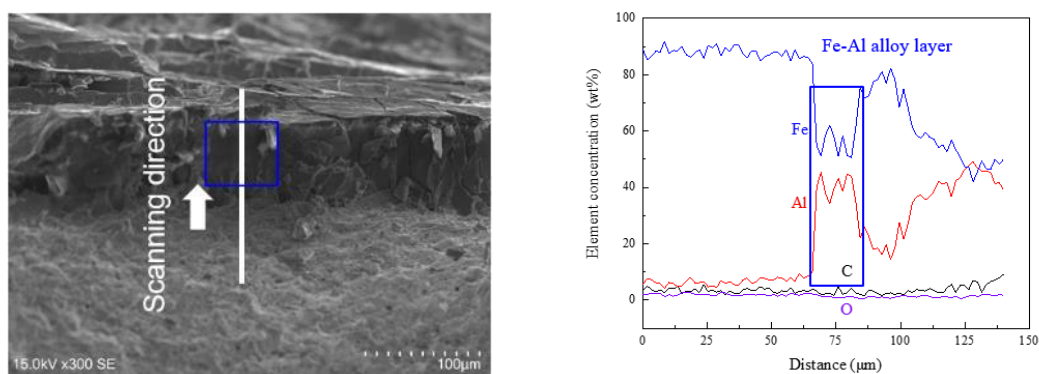


Fig. 7-10 The line analysis of the element in the brittle fracture zone.

shown in Fig. 7-8. From the SEM photos, it is evident that the tensile fracture exhibits obvious ductile fracture from the center to the edge. In the edge zone of the fracture, a brittle fracture, distinct from other areas, is observed with a very smooth surface.

In SEM microscopic observations, an extremely smooth fracture surface morphology was identified. Analysis of the brittle fracture region was conducted under SEM-EDS. The EDS mapping analysis is presented in Fig 6-9, showing an intertwining pattern of aluminum and iron elements in the brittle fracture area. This confirms the occurrence of pronounced brittle fracture phenomena in the alloy layer. Line scanning of the brittle fracture area using SEM-EDS is depicted in Fig 6-10. Both methods yielded consistent mapping results, indicating that brittle fractures occur in the Fe-Al alloy region. The length of brittle fractures is approximately 100 micrometers, concentrated predominantly within all alloy layers.

Cross-linking cracks form in the coating between parallel cracks. This new type of crack, known as inclined cracks or shear cracks, has an inclination angle of approximately 45° with respect to the tensile axis [46,158,159]. The presence of inclined cracks is mainly attributed to the following reasons: under uniaxial loading on the tensile specimen, compressive stresses are induced in another direction due to the Poisson's ratio. In practice, a crack parallel to the loading direction is formed [159]. The maximum shear stress transmitted from the matrix to the coating under uniaxial loading may be large enough to initiate shear failure modes. In fact, inclined cracks are localized by shear action. Fig. 7-11 illustrates the direction of shear stress in the crack coating. In this deformation state, despite the existence of two crack directions on the hot-dip aluminum coating, the layer remains bonded to the substrate. From this, it can be concluded that heat treatment significantly enhances the adhesion between the low-carbon steel matrix and the aluminum coating. Internal cracks are in the final stage at the saturation and delamination levels. Tunnel cracks propagate from the top surface of the coating inward and stop at the substrate [160]. These cracks are widely open and exhibit a planar appearance due to crack opening. Additional transverse cracks parallel to the interface were found in the hot-dip aluminum coating. This result indicates that the adhesion of the film/substrate is too high, and the strength of the hot-dip coating is less than that of the interface [160].

Delamination on the hot-dip aluminum coating may be the result of compressive stresses generated in the coating and tensile stresses generated in the substrate. This compressive stress is initially related to the difference in Poisson's ratio and Young's modulus between the coating and the substrate [161,162]. On the other hand, the observed

delamination in the specimen may be related to high shear stress at the interface. The mechanism of crack formation in the hot-dip aluminum coating may be related to the transfer of shear stress at the interface between the metal substrate during tensile loading. This shear stress reaches a maximum, causing the stress level in the coating to rise to the fracture stress, leading to crack formation [155,163].

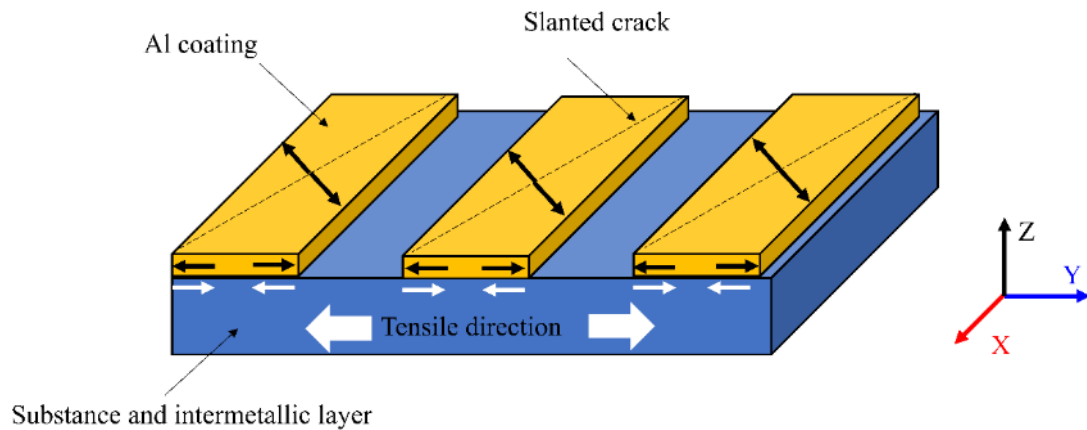


Fig. 7-11 Schematic side view representation of multiple cracking of coatings.

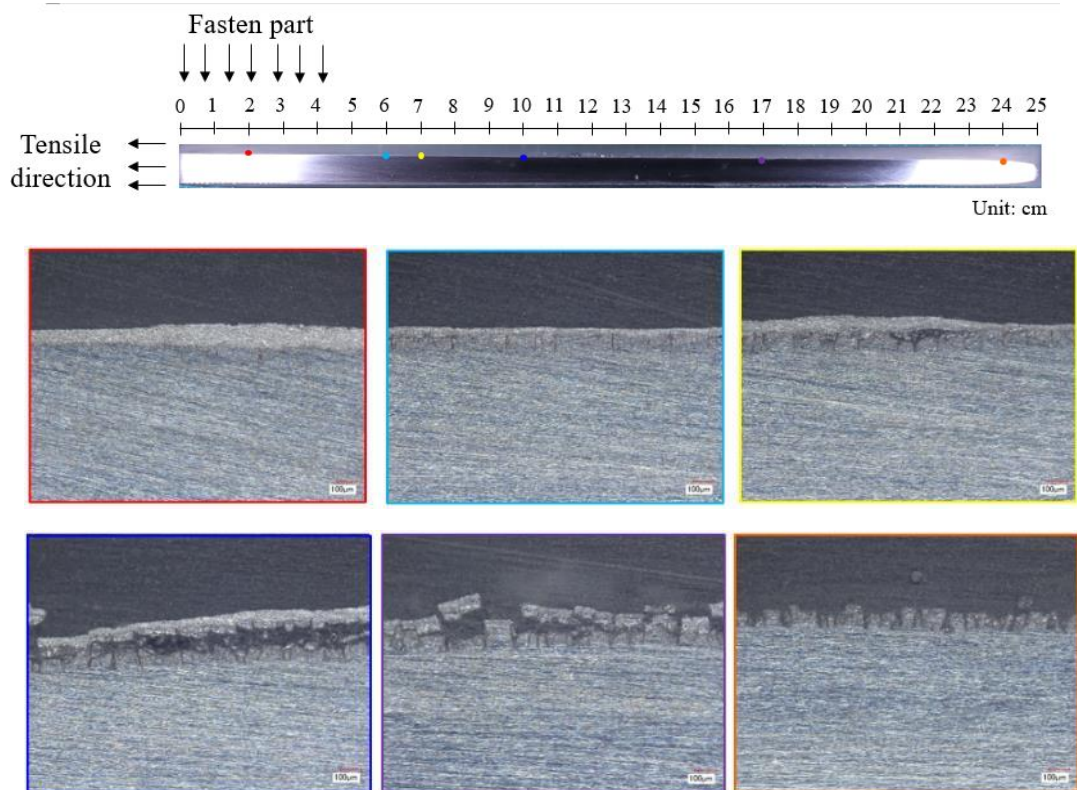


Fig. 7-12 Optical micrographs of cross section hot-dip Al coating on the steel

substrate.

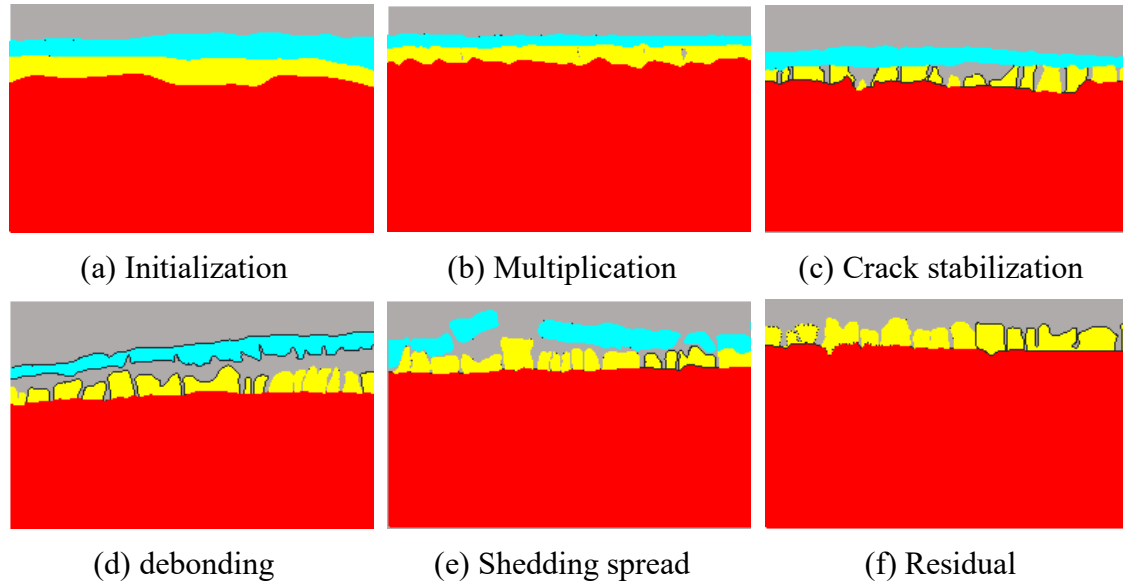


Fig. 7-13 The crack and debonding process of hot-dip Al coating in tensile test.

The evolution of crack density with the prescribed strain is shown in Fig. 7-12. The crack evolution of the specimens can be divided into three stages: initiation, propagation, and stabilization of cracks. In the literature, a higher crack density in the saturation stage indicates stronger adhesion between the coating and the substrate. Coatings with poor adhesion, especially those exhibiting peeling or buckling, typically have lower crack saturation density [46,63]. Referring to the crack density on the coating, shear strain methods are employed to assess the interfacial shear strength of the film/substrate interface. This method relies on the development of vertical crack patterns in brittle films when relatively ductile supports undergo lateral deformation under the action of uniaxial loading [155]. The results indicate that the failure of the hot-dip aluminum coating is initiated by surface vertical cracking, followed by interfacial cracking. No cracks extend into the substrate. Surface vertical microcracks are crucial for coating performance, and their extension is not catastrophic before widespread delamination or peeling occurs [164]. Most microcracks cease to propagate and exist within the coating without reaching the substrate surface, while some microcracks extend within the coating. The crack width increases with the increasing deformation. The maximum crack width is located near the fracture surface, exposing more substrate steel. Almost all crack channels are oriented

perpendicular to the tensile direction. The mid-section bending of crack channels is caused by lateral compression strain resulting from the narrowing of specimen width [160,165]. It can be observed that the substrate steel exhibits ductile fracture, and the cracked coating surface presents a faceted appearance. This indicates that the adhesion of the brittle coating on the ductile steel substrate is approximately reasonable. Additionally, the edges of the coating segments fracture at the interface between the substrate steel and the diffusion layer, suggesting that the diffusion layer is more consistent with the substrate steel than the coating.

The evolution of crack density with the prescribed strain is depicted in Fig. 7-13. The crack evolution of the specimens can be divided into three stages: initiation, propagation, and stabilization of cracks [46,166]. In the literature, a higher crack density in the saturation stage indicates stronger adhesion between the coating and the substrate. Coatings with poor adhesion, especially those exhibiting peeling or buckling, typically have a lower crack saturation density. Referring to the crack density on the coating, shear strain methods are employed to assess the interfacial shear strength of the film/substrate interface. This method relies on the development of vertical crack patterns in brittle films when relatively ductile supports undergo lateral deformation under the action of uniaxial loading. The results indicate that the failure of the hot-dip aluminum coating is initiated by surface vertical cracking, followed by interfacial cracking. No cracks extend into the substrate. Surface vertical microcracks are crucial for coating performance, and their extension is not catastrophic before widespread delamination or peeling occurs [47]. Most microcracks cease to propagate and exist within the coating without reaching the substrate surface, while some microcracks extend within the coating. The crack width increases with the increasing deformation. The maximum crack width is located near the fracture surface, exposing more substrate steel. Almost all crack channels are oriented perpendicular to the tensile direction. The mid-section bending of crack channels is caused by lateral compression strain resulting from the narrowing of specimen width. It can be observed that the substrate steel exhibits ductile fracture, and the cracked coating surface presents a faceted appearance [51]. This indicates that the adhesion of the brittle coating on the ductile steel substrate is approximately reasonable [167]. Additionally, the edges of the coating segments fracture at the interface between the substrate steel and the

diffusion layer, suggesting that the diffusion layer is more consistent with the substrate steel than the coating.

The Young's modulus of the Al-based coating is expected to be only one-third of the steel substrate, while the Young's modulus of the intermetallic layer is similar to that of steel. The consequences are illustrated in the bottom rows of the damage evolution chart. Although the intermetallic phase is brittle regardless of its thickness, thicker joints are expected to initiate cracking at lower strains, with a critical thickness of approximately 3-10 micrometers [168]. Therefore, the hot-dip coating may have undergone plastic deformation before the alloy layer starts to crack [62]. Due to the more ductile nature of the aluminum coating, deformation is expected to occur through ductile shear (at an angle of 45° to the tensile axis), and the resulting shear bands may concentrate stress, serving as the initiation point for cracking, thus shaping the deformation pattern of the coating over the alloy layer's seam [53]. On the other hand, thicker intermetallic compounds are expected to start cracking at lower overall strain levels, i.e., before significant plastic deformation occurs in the aluminum coating and exhibits brittle fracture under normal tensile loading. As these cracks enlarge, they concentrate stress on the ductile but soft aluminum layer, resulting in layer-by-layer failure of the remaining coating at the original position of the first alloy layer crack.

7.5 Summary

In this Chapter, the impact of hot-dip aluminum coating on the mechanical properties of steel was validated through tensile experiments. The study involved a combination of mechanical testing and microscopic observations. From the perspective of experimental data and underlying mechanisms, the research delved into the degradation of steel mechanical properties and the principles of coating failure and debonding. The relevant conclusions are as follows:

- (1) The heat impact generated during the hot-dip aluminum coating process adversely affects the mechanical properties of steel, leading to a reduction in its mechanical performance.
- (2) The cracking of the coating during the hot deformation stage can be attributed to the brittle Fe-Al intermetallic compounds within the coating. The low fracture toughness of Fe-Al intermetallic results in coating cracks nearly perpendicular to the coating/substrate interface.
- (3) The failure of the aluminum coating originates from surface vertical cracks, followed by interfacial cracking. The integrity of the coating is first compromised, leading to coating fracture. The opening of these types of cracks exposes the substrate. With an increase in applied strain, it eventually leads to interfacial delamination of the cracked coating segment.
- (4) The density of surface vertical cracks initially increases with the growth of applied strain. When the substrate reaches critical deformation, there exists a saturation density of cracks.