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Edge Creep of Prepainted Zinc-55% Aluminum Alloy-Coated Steel Sheet

Masashi Takasugi*1 Joji Oka*2

Abstract:

Pretreatments and primers have been studied in series to improve the edge creep resistance of prepainted zinc-55% aluminum alloy-coated steel sheet. According to the results of outdoor exposure tests, the edge creep of prepainted Zn-55%Al alloy-coated steel occurs in the early stages of outdoor exposure, but then gradually declines in the rate of progress, and it is surpassed by that of prepainted galvanized steel at 8 to 9 years. This corrosion mechanism is estimated from the results of EPMA analysis and electrochemical measurement as follows. The cause is the heterogeneous structure characteristic of the Zn-55%Al alloy coating that is composed of a zinc-rich phase and an aluminum-rich phase. In the early stage of exposure, the Al-rich phase is passivated, and the Zn-rich phase is preferentially dissolved anodically to produce a vermiculate form of corrosion. The range of corrosion keeps expanding until the Zn-rich phase is completely lost, when the Al-rich phase begins to corrode. The corrosion product of aluminum, however, accumulates because of it low solubility in water, and thereby retards the corrosion rate of the coating.

1. Introduction

Zinc-55% aluminum alloy-coated steel sheet (trade named Galvalume and coated with a 55% Al-43.4% Zn-1.6% Si alloy) was developed by Bethlehem Steel Corp. of the United States. The Zn-55%Al alloy-coated steel technology was introduced into Japan in 1982, and the product is now manufactured by several steelmakers in Japan. It has at least four times higher corrosion resistance than hot-dip galvanized steel. This excellent corrosion resistance is demonstrated by the results of outdoor exposure tests conducted by Bethlehem Steel and John Lysaght Ltd. of Australia[1-4]. As is well known,however, the Zn-55%Al alloy-coated steel, when prepainted, develops such a drawback, called edge creep, that corrosion creeps under the paint film from the cut edge[5,6]. The edge creep phenomenon must be controlled to a minimum because it badly impairs the commercial value of prepainted Zn-55%Al alloy-coated steel.

Bethlehem Steel Corp. recommends several pretreatments and primers as suited for prepainted Zn-55%Al alloy-coated steel. Few reports are available, however, on the service performance of the product manufactured with the recommended pretreatments and primers.

The authors have conducted several tests on 12 types of pretreatments and 2 types of primers to improve the edge creep

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*1 Kimitsu Works

*2 Technical Development Bureau
(presently Nippon Steel Metal Products Co., Ltd.)

resistance of the prepainted Zn-55%Al alloy-coated steel. The results of outdoor exposure tests over 6 or more years are reported here. To clarify the edge creep mechanism, edge creep portions were examined by electron probe microanalysis (EPMA) and electrochemcal measurement were carried out. The results obtained are briefly discussed herein.

2. Experimental Methods

2.1 Steels

As experimented steel sheets, Zn-55%Al alloy-coated steel made by Bethlehem Steel, Zn-55%Al alloy-coated steel made by Daido Steel Sheet, and hot-dip galvanized steel made by Nippon Steel were used as listed in **Table 1**, all measuring 0.5 mm in thickness. The precoated steels were pretreated as described in Section 2.2, preprimed as described in Section 2.3 and then top coated. The Zn-55%Al alloy-coated steels are available in two types of surface finishes: regular spangle finish and extrasmooth finish with minimum spangle. The hot-dip galvanized steel has zero-spangle finish. The coating weight is 150 g/m^2 for Zn-55%Al alloy-coated steels and 300 g/m^2 for hot-dip galvanized steel.

2.2 Pretreatments

Zinc phosphate treatment, etching-type chromate treatment, dry-in-place chromate treatment, and complex oxide treatment were applied as pretreatments, as listed in **Table 2**.

2.3 Paints

An epoxy primer commonly used on prepainted galvanized steel or a special urethane-modified epoxy primer developed by Daido Steel Sheet for Zn-55%Al alloy-coated steel was applied as primer to a film thickness of 5 to 7 μm. An acrylic paint or a polyester paint was applied as top coat to a film thickness of 12 μm. The details are shown in **Table 3**.

2.4 Outdoor exposure

The specimens were exposure tested in a rural area in Kawasaki. The corrosion resistance of the specimens was evaluated by the paint film creepage from the scribe and the cut edge. The specimens measured 5 by 10 cm.

Table 1 Experimental sheet steels

	Test 1	Test 2	Test 3
Zn-55%Al alloy-coated steel	Regular spangle grade made by Bethlehem Steel (GL-R)	Extrasmooth grade made by Bethlehem Steel (GL-S)	Regular spangle grade made by Daido Steel Sheet (GL-RD)
Galvanized steel	Zero-spangle grade made by Nippon Steel (GI)	Zero-spangle grade made by Nippon Steel (GI)	Zero-spangle grade made by Nippon Steel (GI)

Table 2 Pretreatments

Pretreatment	Steel					
	Test 1		Test 2		Test 3	
	GL-R	GI	GL-S	GI	GL-RD	GI
Zinc phosphate		PB-3305	PB-3305	PB-3305	GR46N-50	PB-3305 GR46N-50
Etching-type chromate	AM-712	AM-712	AM-712	AM712	AM-1310 AL-1225 GRC-68 GR92	AL-1225 GRC-68 GR92
Dry-in-place chromate					AM-1415A AL-NR2-NX AL-NR2-N2	AM-1415A AL-NR2-NX AL-NR2-N2
Complex oxide			MET-1303 MET-3920	MET-1303 MET-3920	MET-3920	MET-3920

Table 3 Paints

Paint	Test 1	Test 2	Test 3
Primer	Epoxy 5 - 7 μm	Epoxy 5 - 7 μm	Urethane-modified epoxy (P01) 5 - 7 μm Special urethane-modified epoxy (P150) 5 - 7 μm
Top coat	Acrylic 12 μm	Acrylic 12 μm	Polyester (F80) 12 μm

Table 4 Electrochemical measurement conditions

Solution	(1) 5% NaCl solution (2) 5% Na_2SO_4 solution (simulating outdoor environment)
Oxygen level	(1) Saturated with oxygen (2) Saturated with air (3) Saturated with nitrogen (simulating underfilm oxygen concentration)
Temperature	20°C

2.5 Investigation of edge creep mechanism

2.5.1 EPMA analysis of edge creep cross section

Samples were taken from the edge creep portions of prepainted Zn-55%Al alloy-coated steel specimens exposed outdoor for 7 years, cross-sectionally examined by microscopy, and analyzed by EPMA.

2.5.2 Electrochemical measurement

The corrosion potential and galvanic current of aluminum and zinc sheets in a galvanic couple were measured as electrochemical variables. As shown in **Table 4**, the electrochemical measurements were made in a common 5% NaCl solution and a 5% Na_2SO_4 solution simulating the atmospheric environment. Given the possibly slow diffusion of oxygen under the paint film, the oxygen concentration was measured at three levels of oxygen, air, and nitrogen saturation to observe the effect of oxygen.

3. Experimental Results and Discussion

3.1 Outdoor exposure performance of prepainted Zn-55%Al alloy-coated steel

3.1.1 First test: 10-year exposure data

Specimens were Zn-55%Al alloy-coated steel sheets (regular spangle) supplied by Bethlehem Steel in 1974. They were treated with an etching-type chromate (AM-712) and coated with an epoxy primer and an acrylic top coating.

Fig. 1 shows the scribe creepage and edge creepage of the exposure test specimens. The scribe creepage of prepainted Zn-55%Al alloy-coated steel is greater than for prepainted galvanized steel during the initial period of exposure (up to 20 months) and then retards. Prepainted galvanized steel has no scribe creepage during the initial period of exposure. It begins

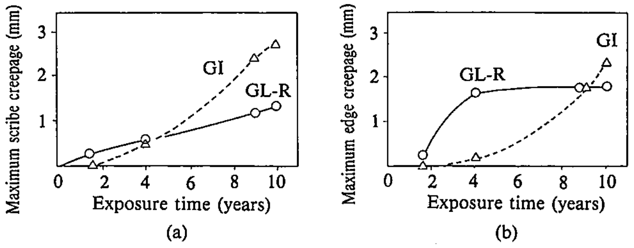


Fig. 1 Change in scribe and edge creepage with time of outdoor exposure: Test 1

GL-R: Prepainted Zn-55%Al alloy-coated steel, GI: Prepainted galvanized steel to develop scribe creepage at 2 years, which catches up with that of prepainted Zn-55%Al alloy-coated steel at 4 years, and surpasses the latter thereafter.

Edge creepage exhibits a similar tendency. The edge creepage of prepainted galvanized steel reaches that of prepainted Zn-55%Al alloy-coated steel at 9 years and surpasses the latter thereafter.

Prepainted Zn-55%Al alloy-coated steel is superior to prepainted galvanized steel in corrosion resistance in the flat sheet condition and has no such spotty blisters as observed on the latter.

3.1.2 Second test: 8-year exposure data

Specimens were Zn-55%Al alloy-coated steel sheets (extra-smooth) supplied by Bethlehem Steel in 1980. They were first treated with zinc phosphate (PB-3305), cobalt complex oxide (MET-1303), etching-type chromate (AM-712), or nickel complex oxide (MET-3920). They were then coated with an epoxy primer and an acrylic top coating.

The measured values of scribe creepage and edge creepage are given in **Fig. 2**. The rust creepage behavior of prepainted Zn-55%Al alloy-coated steel after 8 years of outdoor exposure is similar to that observed after 10 years and described in the previous section. The scribe creepage of prepainted Zn-55%Al alloy-coated steel is greater than for prepainted galvanized steel initially in outdoor exposure (see **Photo 1**), but becomes smaller than for prepainted galvanized steel at 2 years of outdoor exposure.

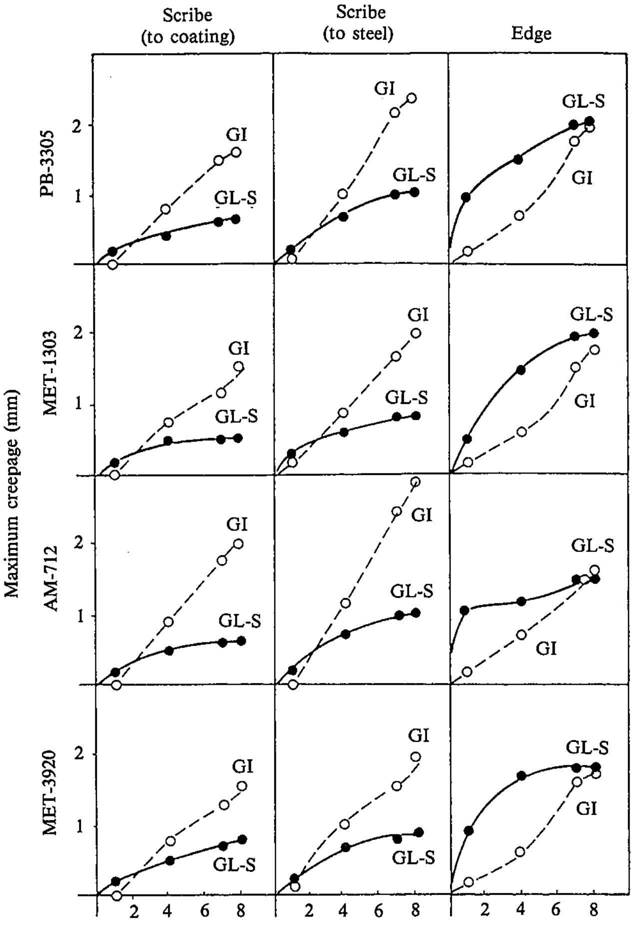
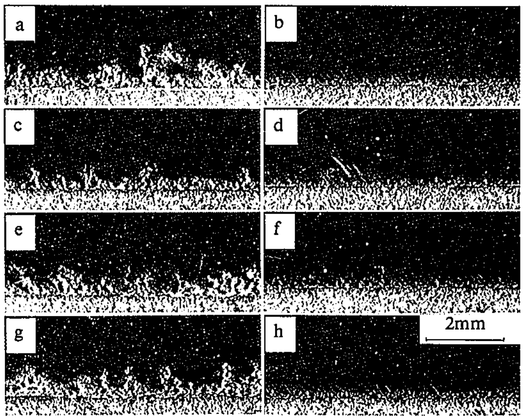
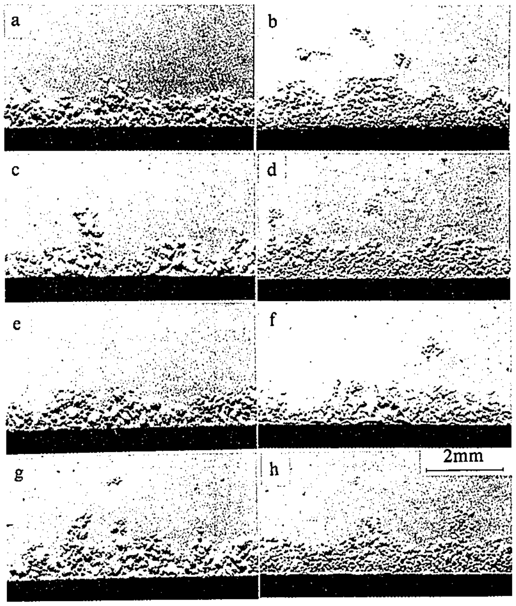


Fig. 2 Change in scribe and edge creepage with time of outdoor exposure: Test 2



a: Zn-55%Al alloy coated (PB-3305) b: Galvanized (PB-3305)
c: Zn-55%Al alloy coated (MET-1303) d: Galvanized (MET-1303)
e: Zn-55%Al alloy coated (AM-712) f: Galvanized (AM-712)
g: Zn-55%Al alloy coated (MET-3920) h: Galvanized (MET-3920)

Photo 1 Edge creep at 1 year of exposure: Test 2



a: Zn-55%Al alloy coated (PB-3305) b: Galvanized (PB-3305)
c: Zn-55%Al alloy coated (MET-1303) d: Galvanized (MET-1303)
e: Zn-55%Al alloy coated (AM-712) f: Galvanized (AM-712)
g: Zn-55%Al alloy coated (MET-3920) h: Galvanized (MET-3920)

Photo 2 Edge creepage at 8 years of exposure: Test 2

The edge creepage of prepainted Zn-55%Al alloy-coated steel is approximately the same as that of the prepainted galvanized steel now at 8 years of outdoor exposure (see **Photo 2**) and is expected to become smaller than that of prepainted galvanized steel in a few years. The difference in the type of pretreatment applied has no appreciable effect on the edge creepage of prepainted Zn-55%Al alloy-coated steel.

3.1.3 Third test: 6-year exposure data

Several of the pretreatments listed in **Table 2** were applied. The paint system consisted of a conventional or special primer and a polyester top coat. The outdoor exposure test results of prepainted Zn-55%Al alloy-coated steel are shown in **Fig. 3**.

The effect of the special primer on the edge creepage at 1 year of outdoor exposure is slightly recognizable when pretreatments

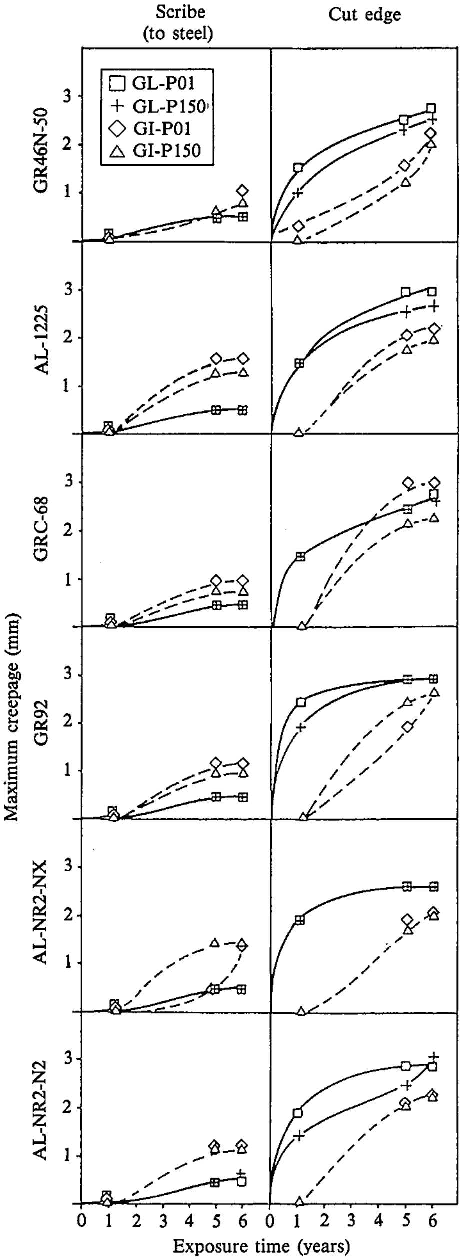


Fig. 3 Change in scribe and edge creepage with time of outdoor exposure: Test 3

are made with GR40N50, GR92, and ALNR2N2. This effect of the special primer diminishes at the 6 years of outdoor exposure, and the difference between the special primer and the conventional primer tends to decrease. The edge creepage of prepainted Zn-55%Al alloy-coated steel, whether coated with the special or conventional primer, is greater than for prepainted galvanized steel. The effect of the pretreatments is not remarkable, but slightly better results are obtained with the GR46N50 pretreatment.

The scribe creepage of prepainted Zn-55%Al alloy-coated steel is smaller than for prepainted galvanized steel. The type of pretreatment and that of the primer are found to have no effect on the scribe creepage of prepainted Zn-55%Al alloy-coated steel.

3.1.4 Summary of edge creep performance

The edge and scribe creepage performance of prepainted Zn-55%Al alloy-coated steel has been discussed above in comparison with prepainted galvanized steel. **Fig. 4** summarizes the edge and scribe creepage data of prepainted Zn-55%Al alloy-coated steel and prepainted galvanized steel.

The experimental data may be summarized as follows:

(1) Prepainted Zn-55%Al alloy-coated steel sustains the edge creep phenomenon earlier than prepainted galvanized steel, with its edge creepage becoming remarkable at 6 to 24 months of outdoor exposure. The edge creep of prepainted Zn-55%Al alloy-coated steel then increases in area but shows down in the rate of progress. The edge creepage of prepainted galvanized steel advances at a constant rate each year and reaches that of prepainted Zn-55%Al alloy-coated steel at 8 to 9 years of outdoor exposure.

(2) The scribe creep of prepainted Zn-55%Al alloy-coated steel occurs earlier than that of prepainted galvanized steel, but is surpassed by the latter at 2 to 4 years of outdoor exposure.

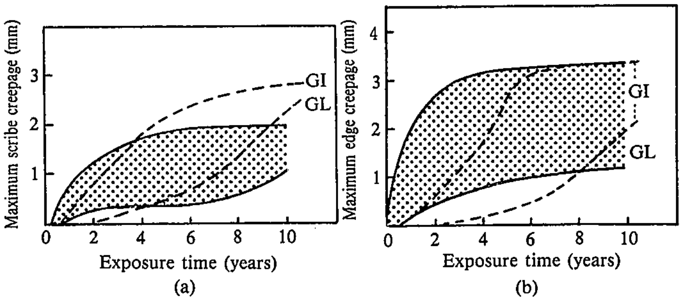
(3) Prepainted galvanized steel has blisters on the flat surface as well after 5 years of exposure. This blister phenomenon is not observed on prepainted Zn-55%Al alloy-coated steel even after 10 years of exposure.

(4) The above results indicate that prepainted Zn-55%Al alloy-coated steel is superior in durability to prepainted galvanized steel.

(5) The edge creepage of prepainted Zn-55%Al alloy-coated steel is difficult to alleviate by improving pretreatment or primer coating.

3.2 Investigation of edge creep mechanism

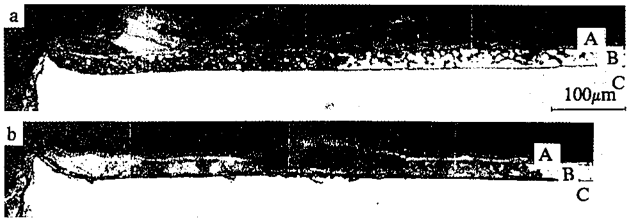
When the edge creep area of prepainted galvanized steel is cross-sectionally examined by microscopy, the corrosion of the galvanized coating is found to proceed almost uniformly from the cut edge, as shown in **Photo 3**. With prepainted Zn-55%Al alloy-coated steel, in contrast, the Zn-55%Al alloy coating is cor-



(a)

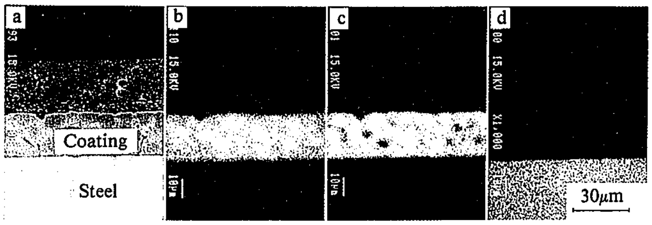
(b)

Fig. 4 Change in scribe and edge creepage with time of outdoor exposure: Tests 1 to 3



a: Zn-55%Al alloy-coated steel, b: Galvanized steel
(A/Paint film, B/Coating, C/Steel)

Photo 3 Cross section through edge creep area at 7 years of outdoor exposure



a: SE image, b: Zn, c: Al, d: Fe

Photo 4 EPMA elemental distribution maps of cross section through prepainted Galvalume steel

roded in a vermiculate pattern under the paint film, and the area of corrosion is wider than for the uniform corrosion of galvanized steel. The corrosion product accumulates at the interface between the paint film and Zn-55%Al alloy coating, and the paint film is pushed up by its buildup, thereby increasing the edge creepage of prepainted Zn-55%Al alloy-coated steel. To clarify this phenomenon that is peculiar to prepainted Zn-55%Al alloy-coated steel, an EPMA of the edge creep area and electrochemical measurement were carried out.

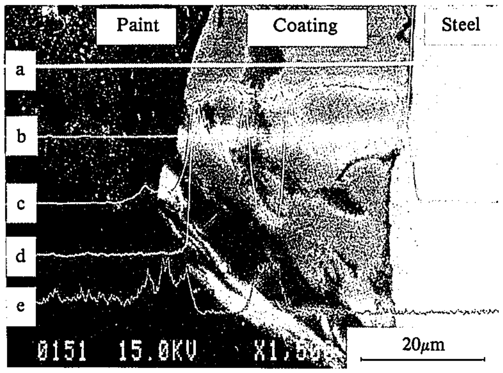
3.2.1 EPMA of edge creep area

Photo 4 shows the EPMA elemental distribution maps of the cross section through the Zn-55%Al alloy coating of prepainted Zn-55%Al alloy-coated steel before the corrosion test. An aluminum-rich phase and a zinc-rich phase are three-dimensionally entangled to form a heterogeneous structure. According to a Bethlehem Steel report, the Al-rich phase is composed of 80% aluminum and 20% zinc, while the Zn-rich phase is composed of 78% zinc and 22% aluminum. The vermiculate-pattern corrosion characteristic of prepainted Zn-55%Al alloy-coated steel may be explained by the local cells that develop and proceed because of the heterogeneous structure of the Al-rich phase and Zn-rich phase.

Photo 5 shows the results of line analysis by EPMA of the cross section through the edge creep area of prepainted Zn-55%Al alloy-coated steel at 7 years of outdoor exposure. Slightly corroded portions (where oxygen is detected in a small amount) are estimated to be the Al-rich phase from the amounts of zinc and aluminum detected. The Zn-rinch phase is high in oxygen detection intensity and extremely low in zinc intensity, so that its corrosion is suggested.

EPMA line analysis was performed at several positions on the cross section through the edge creep area by the method similar to that used to obtain **Photo 5**. In **Table 5**, the sound and corroded portions of the Zn-rich phase are compared in terms of the Al/Zn peak intensity ratio. The Al/Zn peak intensity ratio of corroded portions is greater than that of sound portions. This phenomenon can occur in two cases. One is the preferential dissolution of zinc. In the other case, the corrosion of the Zn-rich phase uniformly proceeds, but as the Zn corrosion product more readily dissolves than the Al corrosion product, the Zn corrosion product runs out of the system, leaving the Al corrosion product in the system.

Photo 6 shows the EPMA elemental distribution maps of the cross section through the edge creep area of prepainted Zn-55%Al alloy-coated steel at 7 years of outdoor exposure. Oxygen is detected where corrosion is confirmed in the scanning electron microscope (SE) image, and the Zn-rich phase with the high X-ray intensity of zinc as shown in **Photo 4** is lost. Aluminum is detected in the corrosion product accumulating at the interface between the paint film and the Zn-55%Al alloy coating, while zinc is hardly recognizable. This is probably because the Zn corrosion product in the Zn-rich phase is more likely to dissolve into rain water than the Al corrosion product.

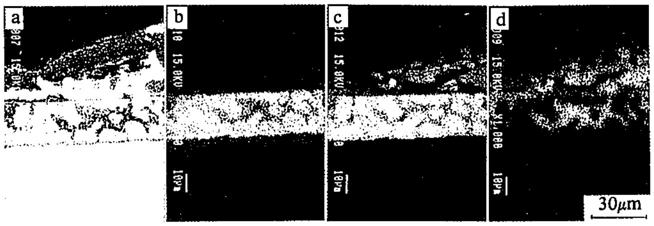


a: Scan line, b: Fe, c: Al, d: Zn, e: O

Photo 5 EPMA line profiles of cross section through prepainted Zn-55%Al alloy-coated steel at 7 years of outdoor exposure

Table 5 Al/Zn ratio determined by EPMA line profile analysis of cross section through prepainted Zn-55%Al alloy-coated steel at 7 years of outdoor exposure

Analyzed portion		Al/Zn ratio			Remarks
		Min.	Max.	Avg.	
Zn-rich phase	Sound	0.03	0.44	0.16	Low oxygen X-ray intensity
	Corroded	0.60	2.10	1.13	High oxygen X-ray intensity
Al-rich phase	Sound	0.40	2.10	1.31	Low oxygen X-ray intensity



a: SE image, b: Zn, c: Al, d: O

Photo 6 EPMA elemental distribution maps of cross section through prepainted Zn-55%Al alloy-coated steel at 7 years of outdoor exposure

According to the above-mentioned EPMA results of the outdoor exposure specimens, the edge creep of prepainted Zn-55%Al alloy-coated steel is preceded by the vermiculate-pattern corrosion of the Zn-rich phase and is caused by the buildup of the resultant Al corrosion product at the interface between the paint film and the Zn-55%Al alloy coating. Since aluminum is less noble than zinc, it is only natural electrochemically that the Al-rich phase should be corroded prior to the Zn-rich phase. To clarify this point, the following electrochemical measurements were made.

3.2.2 Electrochemical measurements

The Al-rich phase and Zn-rich phase of Zn-55%Al alloy-coated steel are microstructural constituents of several micrometers to several tens of micrometers in size. Since electrochemical measurements are difficult to make in each phase or between the two phases, model experiments were run using aluminum and zinc sheets.

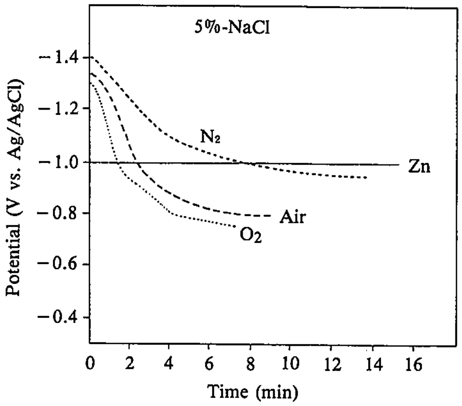


Fig. 5 Change with time in corrosion potential of aluminum and zinc in 5% NaCl solution

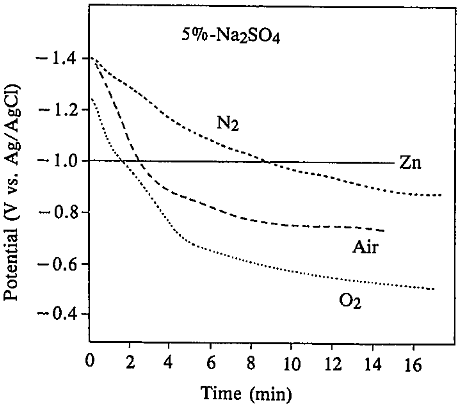


Fig. 6 Change with time in corrosion potential of aluminum and zinc in 5% Na_2SO_4 solution

(1) Measurement of corrosion potential

Figs. 5 and **6** shows the changes with time of the corrosion potential of aluminum and zinc in a 5% NaCl solution and a 5% Na_2SO_4 solution, respectively. Zinc exhibits a corrosion potential of −1.0 V versus Ag·AgCl as soon as it is immersed in the test solution. The corrosion potential of zinc remains unchanged with the lapse of time. As soon as it is immersed in the test solution, aluminum exhibits a corrosion potential of −1.3 to −1.4 versus Ag·AgCl, less noble than that of zinc. The corrosion potential of aluminum becomes more noble with the lapse of time and eventually becomes more noble than zinc. This is probably because an oxide film forms on the surface of aluminum and passivates it[7]. The higher the oxygen concentration of the test solution, the faster changes the corrosion potential of aluminum. As the test solution is not sparged with nitrogen while the corrosion potential is measured, the dissolution of oxygen from air in the test solution is considered to change the corrosion potential of aluminum. The corrosion potential of aluminum changes faster in the Na_2SO_4 solution than in the NaCl solution. This is probably because the formation of a passive oxide film on surface of aluminum in the NaCl solution is retarded by the presence of chloride ions in the solution.

(2) Measurement of galvanic current

Aluminum and zinc were coupled in the 5% Na_2SO_4 solution, and the resultant galvanic current was measured. The results are shown in **Fig. 7**. The flow direction of the galvanic current indicates that aluminum is dissolved as anode immediately after immersion. The galvanic current decreases with the lapse of time. After a certain length of time, the flow direction of the galvanic current is reversed to indicate that zinc has become the anode. The immersion time to the reversal of the flow direction of galvanic current decreases with increasing oxygen concentration in the solution. The time at which the flow direction of galvanic current is reversed agrees with the time at which the corrosion potential of aluminum becomes more noble than zinc in **Fig. 6**.

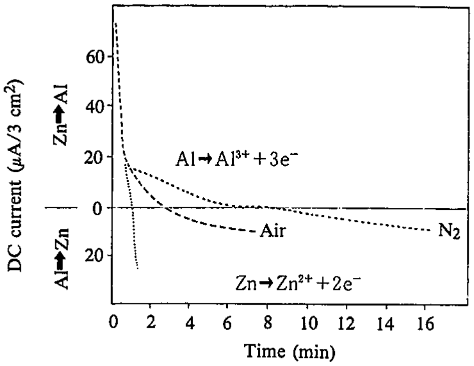


Fig. 7 Change in galvanic current of aluminum-zinc couple in 5% Na_2SO_4 solution

According to the above results, the corrosion of aluminum and zinc is presumed to take the following course: Aluminum is preferentially corroded at first, but at the same time is gradually covered with an oxide film. The oxide film makes the corrosion potential of aluminum more noble. The corrosion of zinc starts when the corrosion potential of aluminum becomes more noble than zinc.

3.2.3 Summary of edge creep mechanism

The electrochemical measurement and EPMA results discussed above suggest that the edge creep of Zn-55%Al alloy-coated steel proceeds through the following stages:

Stage 1: The Al-rich phase, which is electrochemically less noble than the Zn-rich phase, is corroded first.
Stage 2: The Al-rich phase is covered by a thin layer of aluminum corrosion product and is passivated.
Stage 3: The Zn-rinch phase, which is less noble than the passivated Al-rich phase, is corroded. Since the Zn corrosion product is readily dissolved in water and carried out of the system, the corrosion of Zn-rich phase is accelerated.
Stage 4: As soon as the Zn-rich phase is lost, the corrosion of the Al-rich phase is initiated. The Al corrosion product is not readily dissolved in water and accumulates.
Stage 5: The accumulated Al corrosion product has a corrosion protective effect and retards the edge creep rate of Zn-55%Al alloy-coated steel.

4. Conclusions

The edge creep phenomenon of prepainted Zn-55%Al alloy-coated steel was investigated by outdoor exposure tests, and its was studied by means of EPMA and electrochemical measurements. The following conclusions were derived:

(1) The edge creep of prepainted Zn-55%Al alloy-coated steel occurs earlier than that of prepainted galvanized steel and is remarkable at the initial 6 to 24 months of outdoor exposure.

This is attributable to the presence of a heterogeneous structure composed of a Zn-rich phase and Al-rich phase in the Zn-55%Al alloy coating. In the initial stage of corrosion, the Al-rich phase is corroded and passivated, the anodic dissolution of the Zn-rich phase preferentially begins, and the vermiculate-pattern, corrosion of the Zn-rich phase proceeds. The corrosion range of prepainted Zn-55%Al alloy-coated steel is thus considered to be wider than that of galvanized steel.

The edge creep of prepainted Zn-55%Al alloy-coated steel then spreads, but gradually shows down in the rate of progress. As soon as the Zn-rich phase is lost through its vermiculate-pattern, selective corrosion, the Al-rich phase begins to corrode. The Al corrosion product, which does not readily dissolve in water and accumulates under point film is considered to inhibit the corrosion of the Zn-55%Al alloy coating. The galvanized coating is uniformly corroded and dissolved, and its edge creep proceeds at a constant rate. The edge creepage of prepainted galvanized steel surpasses that of prepainted Zn-55%Al alloy-coated steel at 8 to 9 years of outdoor exposure.

(2) The edge creepage of prepainted Zn-55%Al alloy-coated steel can be alleviated slightly by improving pretreatment and prime coating. The resultant edge creepage, however, is still greater than observed for prepainted galvanized steel under the test conditions reported here. This is because the edge creepage of prepainted Zn-55%Al alloy-coated steel heavily depends on the heterogeneous structure peculiar to the Zn-55%Al alloy coating. Improvements in conventional pretreatments and primers are not considered effective enough in drastically reducing the edge creepage of prepainted Zn-55%Al alloy-coated steel. To furthr enhance its overall durability, improvements must be made in the sheet cutting and fabrication methods, while waiting for new pretreatment chemicals and primer systems.

References

1) Zoccola, J.C., Townsend, H.E., Borzillo, A.R., Horton, J.B.: Paper ASTM Symposium on Atmospheric Corrosion, 1976
2) Iezzi, R.A.: Paper NCCA Fall Meeting, 1979
3) Horton, J.B., Borzillo, A.R., Harver, G.J., Reynolds, J.: Paper 6th International Congress on Metallic Corrosion, 1975, Sydney
4) Japan Lead & Zinc Development Association: Lead & Zinc. (92), 15 (1979)
5) Boge, E., Richards, P.N.: Paper Inter ZAC. 81, 1981
6) Fujii, H.: Rust Prevention & Control. 27 (7), 9 (1983)
7) Pourbaix, M: Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, New York, 1966