Technical Report

“55%Al-Zn-2%Mg-1.6%Si Alloy Hot-dip Coated Steel Sheet SGL™” and “Pre-painted SGL” for Building Materials

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Abstract

We developed a 55%Al-Zn-2%Mg-1.6%Si alloy hot-dip coated steel sheet (SGL™). SGL has a similar spangled pattern to the 55%Al-Zn-1.6%Si alloy hot-dip coated steel sheet (GL). The metal coating layer of SGL is formed in Al-rich and eutectic phases. Mg exist as $MgZn_2$ and Mg_2Si in eutectic phase. Superior corrosion resistance by the effect of Mg was confirmed in SGL in both the combined cycle corrosion test and exposure test in comparison with GL. In addition, pre-painted SGL exhibited corrosion resistance superior to pre-painted GL in the combined cycle corrosion examination and exposure examination. Especially in the exposure test, pre-painted SGL was verified as having long-term superior corrosion resistance to that of pre-painted GL in severe corrosion environments such as coastal area and those not protected from rain (under eaves).

1. Introduction

55%Al-Zn-1.6%Si alloy hot-dip coated steel sheets (hereinafter referred to as GL) have excellent corrosion resistance, and are widely used in the building material field as coated steel sheets, and the material sheet for pre-painted steel sheets. In the meantime, in the field of building materials such as roofs and/or walls, there are needs to extend the service life of buildings and/or to use them under severe corrosive environments such as coastal areas. Therefore, demand for further improvement of corrosion resistance is growing.

As represented by Zn-11%Al-3%Mg-0.2%Si alloy hot-dip coated steel sheet (SuperDyma™)[1] and/or Zn-6%Al-3%Mg alloy hot-dip coated steel sheet (ZAM™)[2], Nippon Steel Corporation has established technologies to improve corrosion resistance by making steel sheets coated with the Zn-Al-Mg three-component eutectic phase, in which Mg is added to the coating composition. With the aim of improving the corrosion resistance of GL, Nippon Steel then studied the effect of adding Mg to the GL composition. As a result, we found that the addition of about 2% of Mg to the GL base composition exhibits the highest corrosion resistance improvement,[3] and the 55%Al-Zn-2%Mg-1.6%Si alloy hot-dip coated steel sheet SGL™ (hereinafter referred to as SGL) was developed.

The coating compositions of the SGL and GL coating are shown in **Table 1**.

This article introduces the characteristics and corrosion resistance of SGL coated steel sheet, and the corrosion resistance of pre-painted SGL steel sheet that employ SGL as the material sheet for pre-painting.

2. Characteristics of SGL™ Coating

Figure 1 shows the appearance of coated steel sheets. SGL expresses a spangled pattern like GL, and is characterized by its excellent design. **Figure 2**[3] shows the result of the investigation of a cross section of SGL by an electron probe microanalyzer (EPMA). The coating layer consists of the Al-rich phase principally, and the Zn-rich phase and Mg/Si phase, filling the gaps of the Al-phase. **Figure 3**[3] shows the result of the analysis of SGL by X-ray diffraction (XRD) (radiation source: Cu-Kα). In addition to the peaks of the Al and Zn phases which are observed in conventional GL, the peaks of Mg_2Si and $MgZn_2$ of Mg compounds are observed. This indicates that the SGL coating structure is formed into a three-di-

Table 1 Coating composition in SGL and GL

Sample	Composition			(mass%)	Coating mass
	AL	Zn	Mg	Si	
SGL	55	41	2	1.6	AZ150
GL	55	43	0	1.6	

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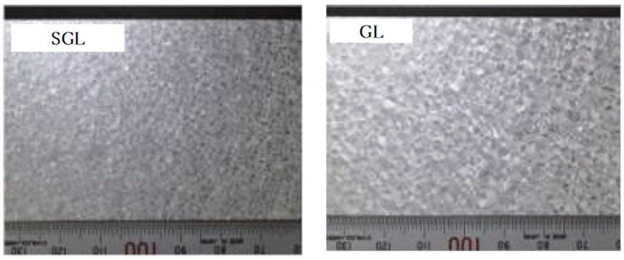


Fig. 1 Appearance of coating steel sheets

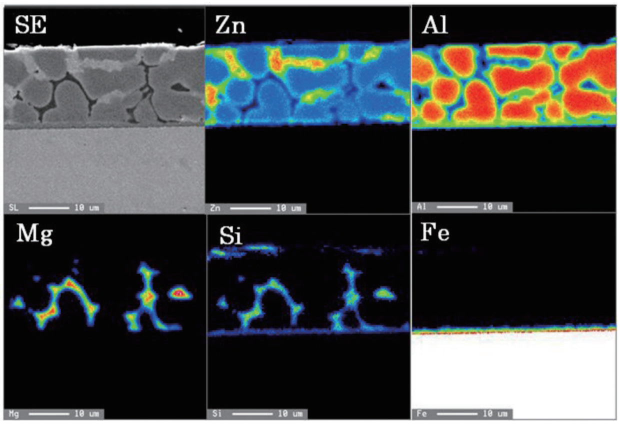


Fig. 2 Sectional element mapping of SGL coating layer by EPMA[3)]

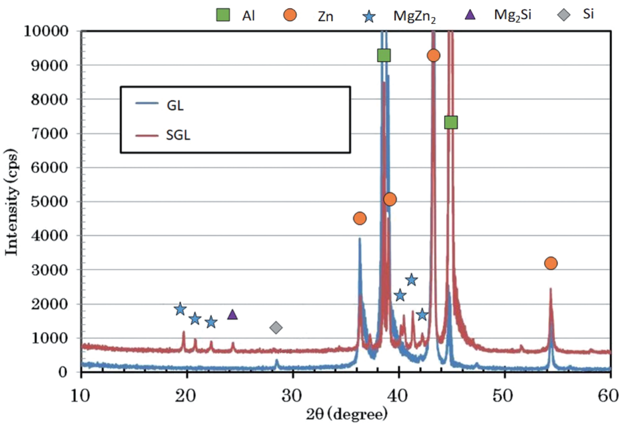


Fig. 3 X-ray diffraction spectrum of SGL and GL[3)]

mensional network structure wherein the Zn-rich phase, $MgZn_2$ phase and Mg_2Si phase fill in the gaps of the Al-rich phase (Al phase).

GL already consists of a three-dimensional network structure of the Al-rich phase and Zn-rich phase. The spangle pattern of GL is also considered to be caused by the growth of Al-rich phase dendrite,[4)] and since SGL has the Al-rich phase as its main phase like GL, a spangle pattern is considered to be expressed similar to GL.

3. Corrosion Resistance of SGL™

3.1 Accelerated corrosion test of SGL™

Figure 4 shows the cycle condition of the 0.5% combined cycle corrosion test (pursuant to JIS H 8502, hereinafter referred to as

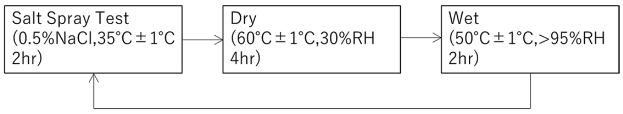


Fig. 4 Conditions for 0.5% CCT

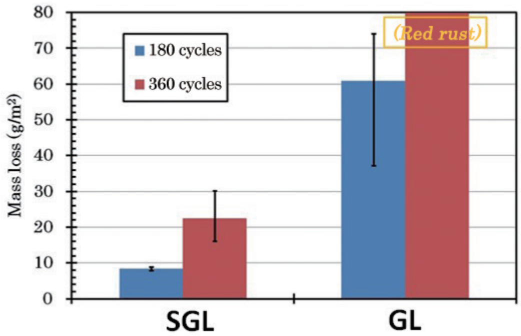


Fig. 5 Mass loss of SGL and GL after 0.5% CCT[3)]

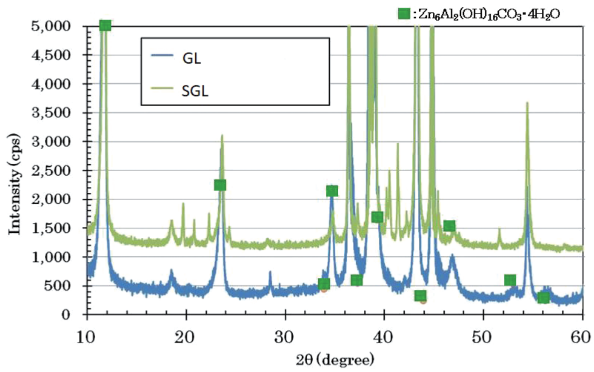


Fig. 6 X-ray diffraction spectrum of SGL and GL after 0.5% CCT[3)]

0.5% CCT). **Figure 5**[3)] shows the mass loss right after 0.5% CCT 180 cycles and 360 cycles. The mass loss of SGL is small, and less than about one third that of GL, and the excellent corrosion resistance of SGL is exhibited. **Figure 6**[3)] shows the result of the XRD analysis right after 0.5% CCT 180 cycles. In both SGL and GL, the $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ peak is confirmed, and no difference is observed in corrosion products. Additionally, in the corrosion products of SGL, the peak that comes from the Mg compound is not confirmed. A preceding study concerning the corrosion behavior of the Zn-Al alloy and Zn-Al-Mg alloy reports that the corrosion products become denser under the existence of Mg even if the constituent phases are the same in both, and high corrosion resistance is obtained.[5)] Although no remarkable difference is observed between the constituent phases of the corrosion products of SGL and GL, the reason for the SGL corrosion resistance being superior is considered to be attributed to the same mechanism.

3.2 Outdoor exposure test of SGL™

For the purpose of evaluating the corrosion resistance under a coastal environment, an outdoor exposure test was conducted in Okinawa Pref. Compared to direct exposure, since a shielded environment not exposed to rain is more robust to the corrosion of metals, specimens were placed in a shielded environment covered by a

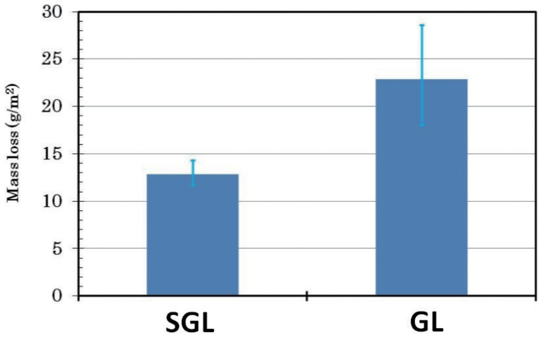


Fig. 7 Mass loss of SGL and GL after outdoor exposure test in Okinawa[3)]

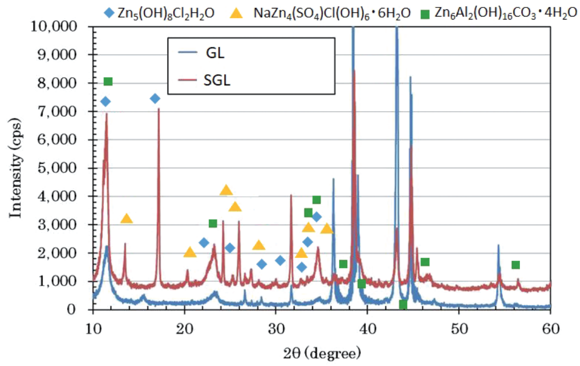


Fig. 9 XRD analysis of SGL and GL after outdoor exposure test in Okinawa[3)]

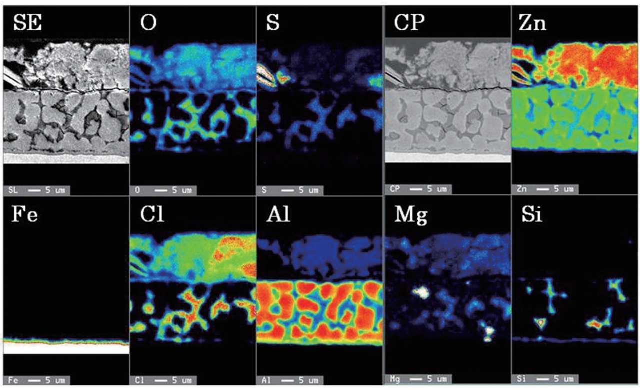


Fig. 8 Cross section of EPMA analysis of SGL coating after outdoor exposure test in Okinawa[3)]

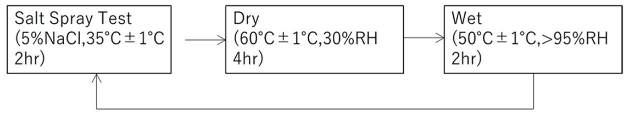


Fig. 10 Conditions for 5% CCT

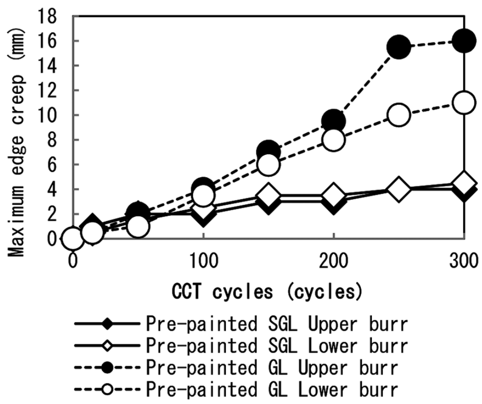


Fig. 11 Time dependence of maximum edge creep in 5% CCT[7)]

roof. **Figure 7**[3)] shows the mass loss of SGL and GL after the one-year exposure test. The mass loss of SGL is smaller than that of GL, and the excellent corrosion resistance of SGL in an outdoor environment is also confirmed. **Figure 8**[3)] shows the result of the analysis by EPMA of the SGL cross section after a one-year exposure. Remarkable corrosion is not recognized in the Al-rich phase of SGL, and it is observed that the corrosion of the Zn-rich phase attributed to the three-dimensional network structure progresses on a priority basis. In addition, the corrosion products are accumulated thickly on the coating layer, and Mg is observed within it. This is considered to be due to rainwater not wetting the specimens directly under a shielded environment, and accordingly the corrosion products are difficult to wash away. In the corrosion products, one region has Zn, Cl and O, and another has Zn, S, Cl and O. It is estimated that chlorides exist in the former region, and that a compound salt of chlorides and sulfates exists in the latter region. **Figure 9**[3)] shows the result of XRD analysis of corrosion products. In SGL, similarly to the accelerated test, $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ is observed, as are $Zn_5(OH)_8Cl_2H_2O$ and $NaZn_4(SO_4)Cl(OH)_6 \cdot 6H_2O$. In GL, $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ and $Zn_5(OH)_8Cl_2H_2O$ are observed.

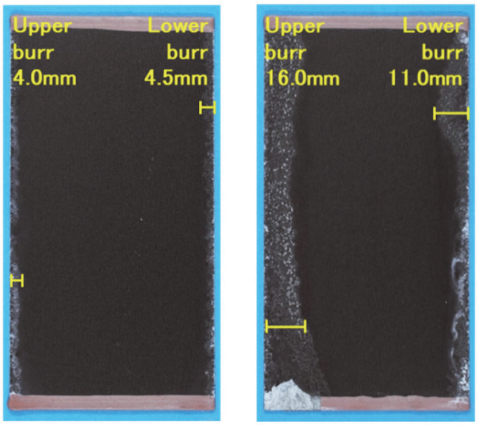
$Zn_5(OH)_8Cl_2H_2O$, a corrosion product having high protective capability, is stabilized by the addition of Mg.[6)] Since the corrosion products of SGL have higher strength than that of GL, similarly to the result of the accelerated corrosion test, corrosion resistance is considered to be improved by the effect of Mg that stabilizes the dense corrosion products that already have high protective capability.

4. Corrosion Resistance of Pre-painted SGL

The corrosion resistance of pre-painted SGL was evaluated, which employed SGL as the material sheet. The pre-painted steel sheet was prepared by coating a chromate-treated SGL (AZ150) sheet 0.35 mm thick with a paint of chromate-type epoxy system resin to a thickness of 4 μm as a primer and a paint of the polyester system to a thickness of 20 μm as the top coat, and then by baking such coated sheet. For comparison purposes, a GL (AZ150) sheet 0.35 mm thick applied with the same treatment and painting was used.

The corrosion resistance of the pre-painted SGL was evaluated by the 5% combined cycle corrosion test shown in **Fig. 10** (pursuant to JIS H 8502, hereinafter referred to as 5% CCT). **Figure 11**[7)] shows the time dependence of the maximum edge creep (the maximum width of the paint blister from the cut edge) up to 300 cycles, and **Fig. 12**[7)] shows the appearance of the specimens at 300 cycles. Compared with that of the pre-painted GL, the edge creeping of the pre-painted SGL is smaller, and the corrosion resistance is superior.

For the purpose of evaluating the corrosion resistance of pre-painted SGL under an actual environment, shaped products of pre-painted SGL and pre-painted GL were installed on the wall of a house in Niigata Pref., and the transition was observed for ten years. **Figure 13** shows the result. The exposure test was conducted in a severe salt-affected area 60 m from the seashore. When we focused on the area under the eaves[8] where specimens are less prone to exposure to rain and corrosion easily progresses, we found that the pre-painted GL exhibited spot-like white rust on the flat surfaces

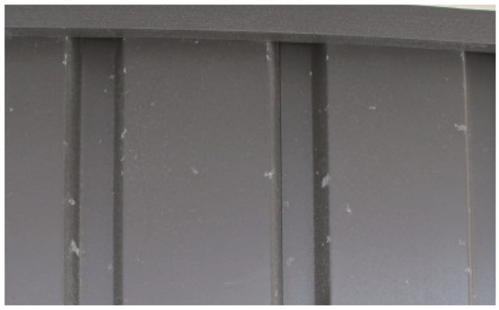
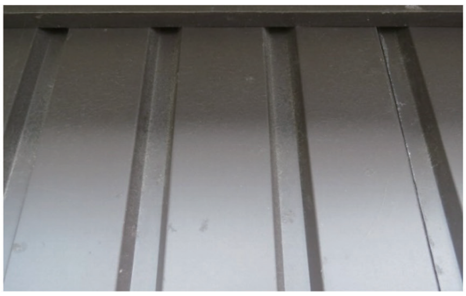
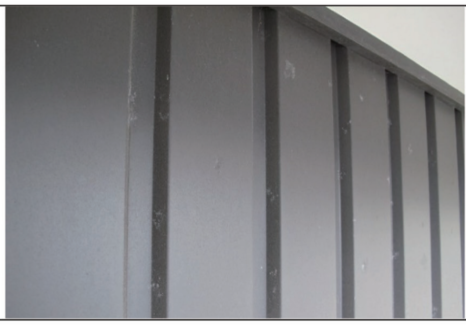
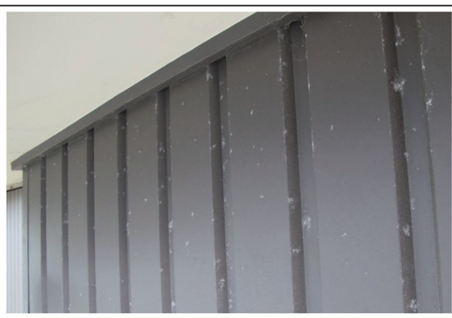


(a)Pre-painted SGL (b)Pre-painted GL

Fig. 12 Appearance of the specimens after 5% CCT for 300 cycles[7]

(a) Complete view

Fig. 13 Results of field exposure test in Niigata (outer wall under eaves)

	Pre-painted SGL	Pre-painted GL
3 years		
5 years		
10 years		

(b) Results of observation

Fig. 13 Results of field exposure test in Niigata (outer wall under eaves) (continued)

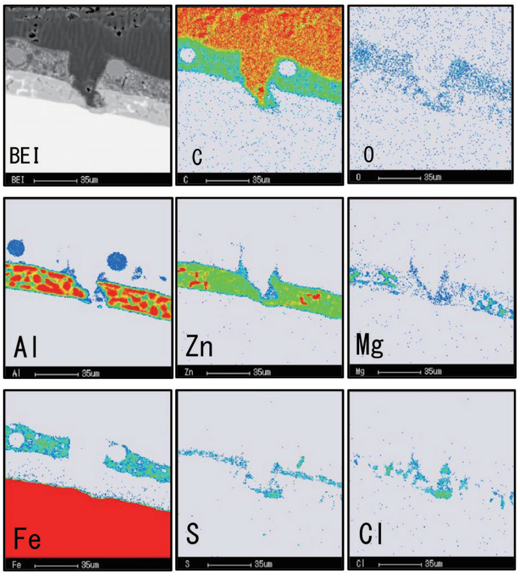


Fig. 14 SEM images and element mapping images of bending cross-section area in outdoor exposure specimens (5 years)

and bending parts two to three years after installation, while on the other hand, the pre-painted SGL exhibited almost no white rust, indicating that the progress of corrosion was suppressed. The difference was more obvious after five years, and the superiority of pre-painted SGL remained unchanged after ten years. From the results of the outdoor exposure test under an actual condition, it was confirmed that pre-painted SGL has excellent corrosion resistance over a long period of time.

To investigate the corrosion state of pre-painted SGL, a portion of a specimen under the eaves (non-rain-exposed area) was sampled five years after installation, and the cross section of the bending part was observed and analyzed by scanning electron microscopy (SEM) and an electro probe microanalyzer (EPMA) (wavelength dispersive X-ray analysis: WDX). The result is shown in **Fig. 14**. The corrosion products that contain the coating elements of Zn and Mg are distributed over the cracks developed on the painting film and coating film at the bending part developed by shaping work. As stated in Paragraph 3.2, this suggests the improvement of corrosion resistance by the effect of Mg densifying the corrosion products of the Zn system. This phenomenon is assumed to be similar to the undercoating corrosion that occurs on flat surfaces. Therefore, it is considered that the corrosion resistance of pre-painted SGL is superior to that of pre-painted GL in both flat and bending parts over a long period of time.

5. Conclusion

The SGL coating surface is spangled similarly to GL, and therefore, its coating structure is confirmed to consist of the Al dendrite and eutectic phase. Mg is present in the eutectic phase in the form of $MgZn_2$ and Mg_2Si, and it is confirmed that, both in the accelerated corrosion test and the exposure test, SGL exhibits corrosion resistance superior to that of GL. This is considered to be attributed to the formation of densified corrosion products in the coating effectuated by Mg, and the corrosion resistance is improved thereby.

Pre-painted SGL exhibits corrosion resistance superior to that of pre-painted GL both in 5% CCT and outdoor exposure tests. In the exposure test in particular, despite being in a very severe corrosive environment close to the seashore and under eaves (non-rain-exposed area), the corrosion resistance of pre-painted SGL maintained its superiority over that of pre-painted GL for a long period of time.

We expect the applications of SGL and pre-painted SGL will be further advanced hereafter to building material usage that requires higher corrosion resistance.

References

1) Morimoto et al.: Tetsu-to-Hagané. 89 (1), 161 (2003)
2) Komatsu et al.: Tetsu-to-Hagané. 86 (8), 534 (2000)
3) Fujii, S., Shimoda, N.: Galvatech 2015
4) Yasuda et al.: Creation and Nano Analysis of High Function Hot-dip Galvanizing Coating Film, Okayama, 2019-09, Iron and Steel Institute of Japan
5) Shinozaki et al.: Journal of The Institute of Metals and Materials. 73 (7), 541 (2009)
6) Uranaka et al.: Nisshin Seiko Giho. (92), 9 (2011)
7) Sugitani: The Iron and Steel Institute of Japan, 170th Autumn Meeting, Fukuoka, 2015-09
8) Takata et al.: Japan Association of Corrosion Control Technology Meeting, 37 (2016)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