

## Effect of Heat Treatment on Corrosion Resistance of Zn-Mg-Al Alloy Coated Steel

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Hot-dip Zn-Mg-Al coatings have a complex microstructure consisting of Zn, Al, and MgZn<sub>2</sub> phases. Its crystal structure depends on alloy content and cooling rates. Microstructure and corrosion resistance of these coatings might be affected by heat treatment. To investigate effect of heat treatment on microstructure and corrosion resistance of Zn-Mg-Al coatings, Zn-1.5%Mg-1.5%Al coated steel was heated up to 550 °C at a heating rate of 80 °C/s and cooled down to room temperature. At above 500 °C, the ternary phase of Zn-MgZn<sub>2</sub>-Al was melted down. Only Zn and MgZn<sub>2</sub> phases remained in the coating. Heat- and non-heat-treated specimens showed similar corrosion resistance in Salt Spray Test (SST). When a Zn-3.0%Mg-2.5%Al coated steel was subjected to heat treatment at 100 °C or 300 °C for 200 h and compared with GA and GI coated steels, the microstructure of coatings was not significantly changed at 100 °C. However, at 300 °C, most Al in the coating reacted with Fe in the substrate, forming a Fe-Al compound layer in the lower part of the coating. MgZn<sub>2</sub> was preferentially formed in the upper part of the coating. As a result of SST, Zn-Mg-Al coated steels showed excellent corrosion resistance, better than GA and GI.

**Keywords:** Zn-Mg-Al coating, Heat treatment, Corrosion, Phase transformation, MgZn<sub>2</sub>

### 1. Introduction

The application of Zn-Mg-Al coated steel is expanding due to its superior corrosion resistance compared to conventional Zn coated steel, such as GA and GI [1-3]. This type of coated steel is used in structural materials for buildings, as well as in the interior and exterior panels of automobiles where corrosion resistance is necessary. It has also been increasingly used in premium home appliances [2,3]. This coating greatly enhances corrosion resistance while reducing the amount of coating required. As a result, it helps protect the environment by reducing the consumption of natural resources and extending the product's lifespan. Its advanced anti-corrosion properties are caused by self-forming protective oxides called

simonkolleite and double hydroxide (LDH) on the surface as shown in Fig. 1. These are mainly due to Mg effects in the coating [4-7]. Corrosion resistance may be reduced if the coating is thermally damaged. However, the thermal effects on the coating have not been studied in detail. Thermal damage can be caused by higher temperatures with shorter exposure times, such as in the heat-affected zone during welding, or by prolonged exposure to temperatures in the 300 °C range, such as in boilers or machine rooms. This study investigates thermal effects on coating phases and corrosion resistance of Zn-1.5%Mg-1.5%Al and Zn-3.0%Mg-2.5%Al (% means wt% in this article) coated steels. The following two cases are assumed to be thermal conditions. The first is a relatively high temperature for a short period of time, resulting in melting of the coating layer. The other condition is to maintain a relatively low temperature below the melting point of the coating for a long time. The phase transformation of the coating is studied. The corrosion resistance is evaluated with and without the heat-affected specimens.

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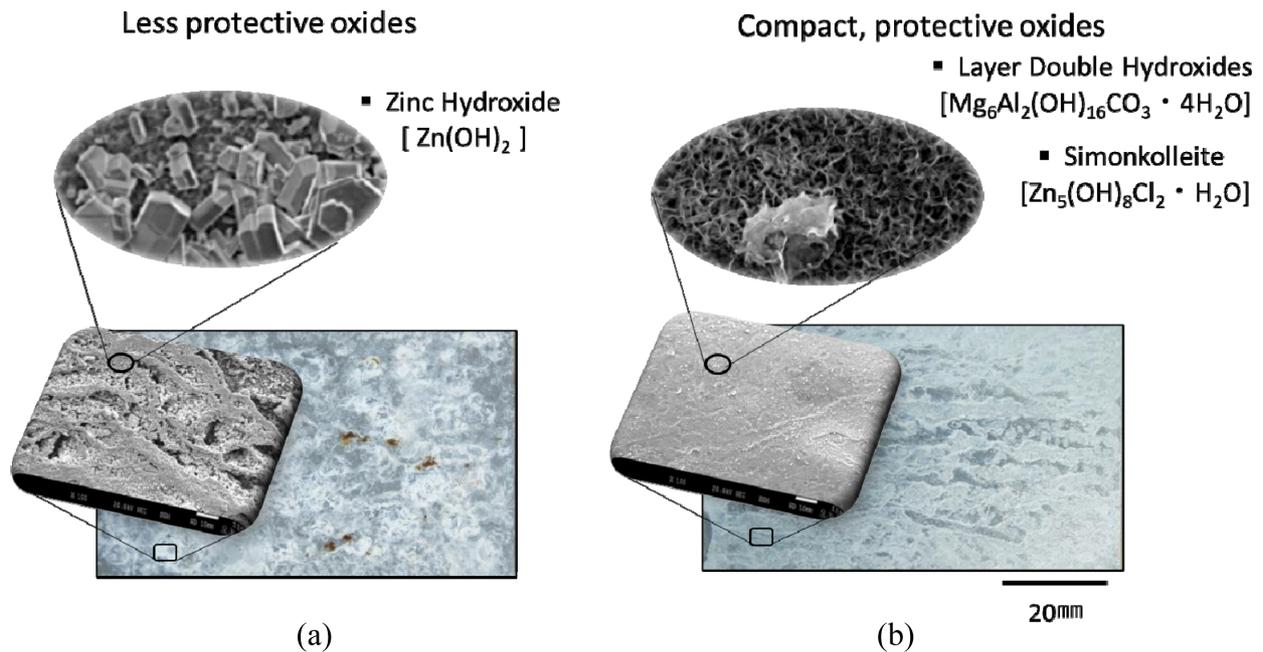


Fig. 1. Surface appearance & SEM images after Salt Spray Test (SST) in 110 h GI 70g, (b) Zn-1.5%Mg-1.5%Al 70g

## 2. Experiment

The heat treatment experiments were carried out in air in two different ways. The first experiment was an evaluation of the effect of rapid heating to 550 °C in a short period of time. The heating temperature was lowered in 50 °C intervals down to 350 °C. The Gleeble tester was used for heating tests on Zn-1.5%Mg-1.5%Al coated steel. The coating amount is 70 g/m<sup>2</sup> per side. The heating rate is 80 °C/s, and then the temperature is held for 10 s. The specimen was then cooled to room temperature at a rate of 5 °C/s. Thermocouples were attached to the specimen to control the exact temperature of the specimen. The detailed thermal cycle is shown in Fig. 2. The coating phases were analyzed by EPMA and XRD. The tested specimens were evaluated for corrosion resistance using the Salt Spray Test (SST) according to ISO9227 [8]. An unheated specimen is tested simultaneously as a reference. In the second experiment, the Zn-3.0%Mg-2.5%Al coated steel was heat treated at 100 °C and 300 °C for 200 h, the coating weight is 50 g/m<sup>2</sup> per side. GA and GI steel sheets were used as reference materials. The coating weights were 45 g/m<sup>2</sup> and 70 g/m<sup>2</sup>, respectively. The Al content in GI is 0.21% and in GA is 0.11%. After heat treatment, the cross sections of the specimens were analyzed by

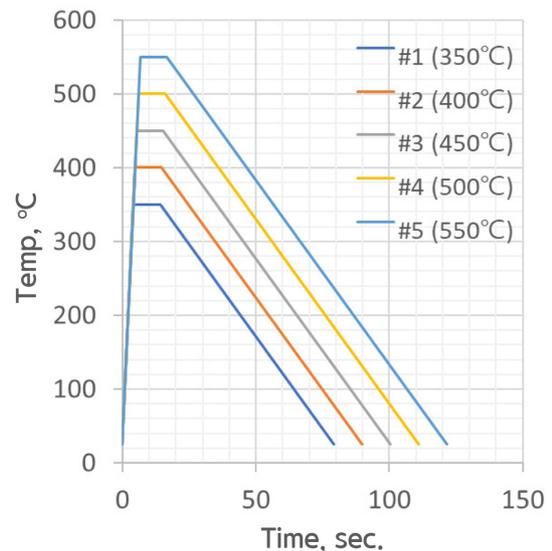


Fig. 2. Experimental conditions for rapid heat treatment

EPMA and the changes in the coating phases were examined by XRD. And the corrosion resistance was evaluated with each other by SST.

## 3. Results

Fig. 3 shows the appearance of the specimens after the rapid heating tests from 350 to 500 °C. Up to 500 °C no

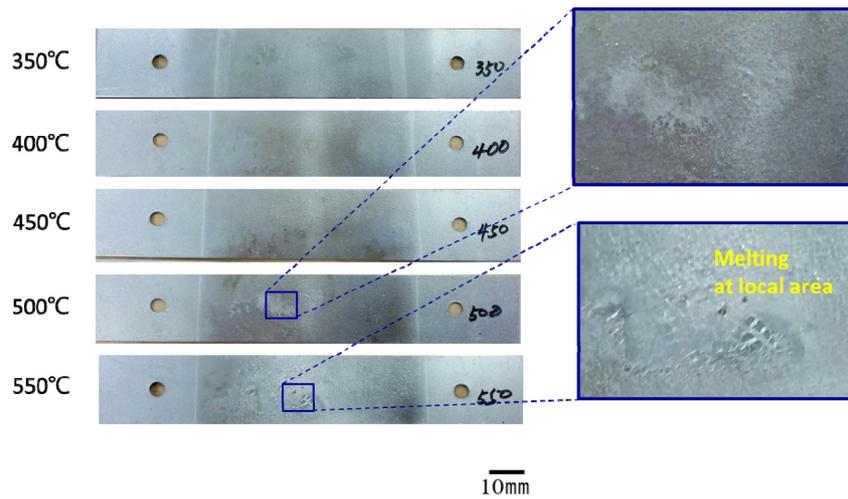


Fig. 3. Appearance figures of heat-treated Zn-1.5%Mg-1.5%Al specimens in 350 ~ 550 °C for 10 s

significant melting is observed on the surface. However, at a temperature of 550 °C, some traces of melting are observed on the specimen. From a thermodynamic point of view the composition Zn-1.5%Mg-1.5%Al is completely melted at 391 °C [2]. In this experiment, however, the melting that can be observed begins at 550 °C. It is believed that the amount of heat applied to the coating layer was less than the melting latent heat of the coating due to the short heating time in this experiment.

Fig. 4 shows the cross sections with EPMA element maps of the specimens heated to 450 °C and 500 °C. The phase ratios are analyzed by XRD. They are showed together. The specimen heated at 450 °C shows that the coating is composed of ternary phases of Zn, MgZn<sub>2</sub> and Al. This coating structure and phases are basically the same as in the unheated specimen. In the specimen heated to 550 °C, the cross section of the coating structures is not different from that of the untreated specimen. However, the EPMA element map shows a significant reduction of Al in the coating. It is observed that Al is concentrated at the interface. XRD analysis also shows no Al phase in the coating. The Zn-1.5%Mg-1.5%Al coating consists of 3 phases; a single phase of Zn, a binary phase of Zn-MgZn<sub>2</sub>, and a ternary phase of Zn-MgZn<sub>2</sub>-Al. Each phase has a different melting point. The lowest is the Zn-MgZn<sub>2</sub>-Al phase, which is 341 °C [2,3]. When heat treated at 550 °C, partial melting occurred in the coating, and it is believed that the ternary phase melted first. It is assumed that the molten Al phase partially dissolves into the Zn phase and partially migrates to the

	450°C	550°C
Image		
Al Map.		
Mg Map.		
	XRD Phase(%)	XRD Phase(%)
Zn	71.8	93.7
MgZn <sub>2</sub>	6.2	6.3
Al	22.1	0

Fig. 4. EPMA element mapping and XRD results for the tested specimens at 450, 550 °C

interface of the coating layer and the steel substrate. The growth of the inhibition layer would be a result of the migration of Al to the interface. In this study, heat treatment up to 500 °C showed no significant difference in the phases of the untreated coating. However, at 550 °C, the Al-containing alloying phase in the coating decomposed to

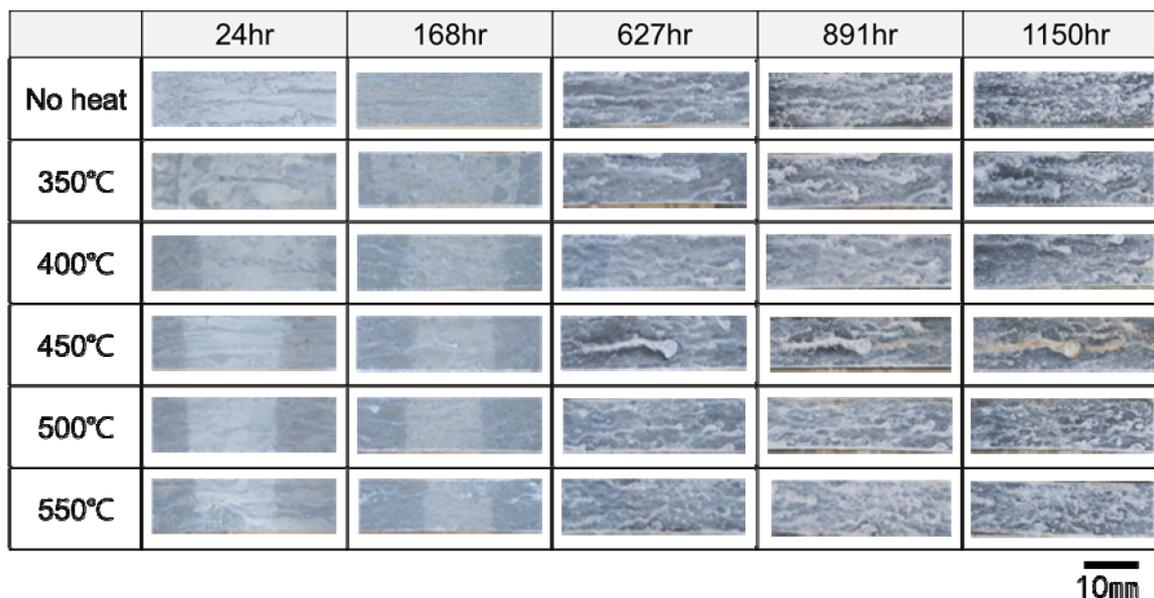


Fig. 5. Appearance of specimens evaluated by SST after heat treatment

form a FeAl compound at the interface.

In order to evaluate the corrosion resistance of the heat-treated specimens, the SST corrosion test was carried out for up to 1,150 h, and the appearance of the specimens is shown in Fig. 5. White rust increased on the specimen surface with increasing corrosion time. The development of white rust was independent of the heating temperature. No effects of heat treatment were observed in this corrosion evaluation experiment. It was assumed that the surface was protected by a stable simonkolleite layer [5-7], which played an important role in improving the corrosion resistance, since the Mg content in the coating layer was maintained under the heat treatment conditions of this study.

In the second part of this study, the phase transformation and the corrosion resistance of the Zn-3.0%Mg-2.5%Al coating were investigated after 200 h of heat treatment at 100 and 300 °C. Fig. 6 shows cross sections of the coating and its EPMA element maps after heat treating. After heat treatment at 100 °C, the phase structure of the coated layer is not different from that of the untreated specimen. However, a significant phase change is observed at 300 °C. This is due to the diffusion of the coating components. For both GA and GI coatings, it can be seen that Zn diffuses deeply along the grain boundaries of the steel substrate. The Al element map of the GI coating shows that the inhibition layer has partially disappeared.

In the case of GA and GI, the mutual diffusion of Zn and Fe occurs when the inhibition layer is destroyed during heat treatment at 300 °C. In the case of Zn-3.0%Mg-2.5%Al coating, the coating layer was decomposed and a new phase was formed. At the interface between the coating and the steel substrate, a thick Fe-Al alloy layer was formed. Most of the Al in the coating is concentrated at the interface. It forms a thick diffusion barrier of Fe-Al compounds. As a result, there is no diffusion of Zn into the substrate. Mg migrates to the top of the coating layer to form MgZn<sub>2</sub>. Thermodynamically, the phases in the ZnMgAl coating were stable at 300 °C [2,3]. As shown in the results of the short-heating time in Fig. 4, there was no phase transformation at 300 °C. However, with prolonged heat treatment at 300 °C, both binary and ternary phases decomposed. As a result, Mg and Al migrated to the formation of new phases.

Despite the degradation of corrosion resistance observed in all samples under 300 °C preheating conditions, the ZnMgAl alloy coating still demonstrated superior performance compared to GA and GI coatings. This superiority can be attributed to the formation of a thick Fe-Al alloy layer at the interface, which acts as a robust diffusion barrier, preventing the penetration of corrosive elements into the substrate. Additionally, the migration of Mg to the top of the coating layer to form MgZn<sub>2</sub> contributes to the formation of a protective layer that

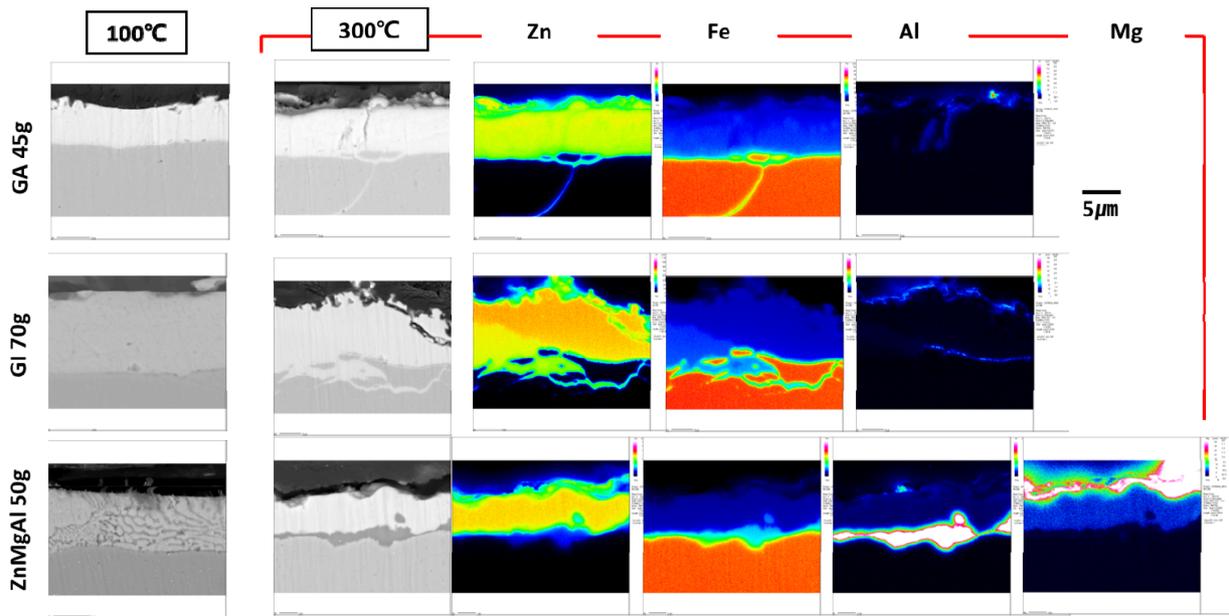


Fig. 6. Cross sections and EPMA element mapping of specimens heat treated at 100 °C, 300 °C for 200 h

Coating	SST 300hr	
	Preheat at 100°C for 200hr	Preheat at 300°C for 200hr
GA 45g		
GI 70g		
Zn-3.0%Mg-2.5%Al 50g		

30mm

Fig. 7. Appearance of heated specimens after SST corrosion test for 300 h

enhances corrosion resistance. Therefore, even though there is some degradation, the overall structure and composition of the ZnMgAl coating provide better protection against corrosion.

Fig. 7 shows the appearance of the specimens after the

300 h SST corrosion evaluation for the specimens heat treated at 100 and 300 °C. In the case of GA, red rust spread over most of the surface after 100 h of heat treatment. In the case of GI, the red rust appeared partially on the specimen after 100 h of heat treatment. After 300 h,

however, the red rust covered most of the surface. In the case of the Zn-3.0%Mg-2.5%Al coating, no red scale appeared on the sample heated to 100 °C. The sample heated to 300 °C showed some red staining. However, the amount of red staining was much less than that of GI or GA. When heat-treated at 300 °C for 200 h, all of the tested specimens show deterioration in corrosion resistance compared to unheated specimens. However, the ZnMgAl alloy coating is superior to GA or GI in terms of corrosion protection.

#### 4. Conclusions

In this study, the thermal effects on Zn-Mg-Al coatings in an industrial environment were investigated.

No phase change was observed in the Zn-1.5%Mg-1.5%Al coating layer when heated up to 500 °C for a short-heating time of less than 10 seconds. However, at temperatures above 500 °C, the phases decomposed. Despite this, there was no significant change in corrosion resistance.

For the Zn-3.0%Mg-2.5%Al coating, heat treatment at 300 °C for 200 h resulted in decomposition of the coating phases. However, compared with GA and GI coatings, it showed superior corrosion resistance even after heat treatment.

It is expected that the corrosion resistance of ZnMgAl coatings, even under thermal effects, will be superior to that of conventional Zn coatings such as GA and GI.

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