NIPPON STEEL & SUMITOMO METAL TECHNICAL REPORT No. 108 MARCH 2015

Technical Report

UDC 669 . 14 - 408 . 2 : 669 . 586 . 5 : 669 . 55 ' 71 ' 721

Corrosion Resistance of Several Zn-Al-Mg Alloy Coated Steels

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Abstract

Hot dip galvanized steel sheets are used in many fields including building materials for the excellent corrosion resistance property. Recently, hot dip galvanized steel sheets adding Al or Mg have been developed and are being used for further enhancing the level of corrosion resistance. In this report, the changes in the levels of corrosion resistance are compared as the amount of Al and Mg is changed, and it is demonstrated that the higher the Al%, the longer the corrosion resistance lasts, that the addition of Mg significantly enhances the level of corrosion resistance, and that the optimal amount of Al% should be more than 6-8% and that of Mg should be 3%.

1. Introduction

Hot-dip galvanized steel sheets are widely used in many fields such as automobile, civil engineering, and building materials, owing to its excellent corrosion resistance. In the fields of civil engineering and building materials in particular, hot-dip galvanized steel sheets with a coating weight of 180 g/m^2 or above on both sides together is used in many cases, and under a severely corrosive environment like the one on a coastal area in particular, corrosion resistance is insufficient in many cases. Thus, an improvement in corrosion resistance to prolong the life of materials has been sought for. To meet this demand, hot-dip Zn-5mass% coated steel sheet (hereinafter referred to as "%" instead of mass%)-Al system wherein corrosion resistance was enhanced by adding aluminum to zinc has been put into practical use. Hot-dip Zn-5mass% coated steel sheet system have bare corrosion resistance that is better by more than two times than that of hot-dip galvanized steel sheets in salt spray testing (hereinafter referred to as "SST").[1)]

However, in recent years, the requirement of galvanized steel sheets with greater corrosion resistance has grown from the viewpoint of prolonging the life of buildings including houses, and commercialization of Mg-added galvanized steel sheets of Zn-11%Al-3%Mg-0.2%Si (hereinafter referred to as "SD") and Zn-6%Al-3%Mg has been promoted since before,[2, 3)] and are mainly and widely used as sheet material in the field of building. Mg-added galvanized steel sheet of this type was registered with Japanese Industrial Standard (JIS) as "G 3323" in November, 2012.

Movement of developing commercialization of Mg-containing galvanized steel sheet is accelerated in recent years, and Mg-added galvanized steel sheets of Zn-Al system with Al mass of 1%–3.5% is being developed, not being limited to building material only but with automotive field in sight.[4-6)] The primary crystal of the coating forecast based on the equilibrium diagram is Zn and the primary crystal of the coating containing Al of 6% or above is Al, and therefore, there is a possibility of a difference in properties. Then, the result of evaluation of plane corrosion resistance of various Zn-Al-Mg-Si coated steel sheets is reported.

2. Method of Experiment

2.1 Preparation of coated steel sheet test samples

Coated steel sheet test samples were prepared in the following manner: ultra-low carbon steel sheet of thickness of 0.8mm was annealed in reducing atmosphere (N_2-5%H_2, dew point −40°C, 800°C × 60s), and hot-dip-galvanized at entry speed of 500 mm/s, at entry sheet temperature of 10°C + bath temperature, dipped for 3 seconds in the bath of aimed compositions (bath temperature: 450°C). The drawing speed was 150 mm/s and the coating weight was controlled to 90 g/m^2 on either side by N_2 wiping.

2.2 Corrosion test and analysis

Plane corrosion resistance of the coating of the prepared samples was evaluated by 5%NaCl JASO-CCT method. The plane part was evaluated at 15th cycle, 30th cycle, and 45th cycle through observation of the appearances of the coating, corrosion mass loss, X-ray diffraction (XRD), and observation of the cross sections.

3. Result and Discussion

3.1 Removing methods of corrosion product

As a removing methods of corrosion product of Zn-Al-Mg coating, dipping the test samples for 15 min at room temperature in the water

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solution of ammonium dichromate = 20 g, 500 ml of 30% ammonia aqueous solution and 500 ml of distilled water (hereinafter referred to as “Method-1”) was employed. Among the methods of separating corrosion product of Zn coated steel sheet specified in ISO8407-2009, the frequently used method of dipping for 1 min in 20% water solution of chromic acid (CrO_3) (80°C) (hereinafter referred to as “Method-2”) exerts great damage not only to the corrosion product but also to the Mg-containing coating itself. **Figure 1** shows the mass loss of uncorroded SD and Zn-0.2%Al (hereinafter referred to as “GI”) after being dipped under a designated condition (hereinafter referred to as “Blank loss”).

Either coating shows greater blank loss in Method-2 than in Method-1 and it is found that the mass loss is more remarkable in high Al-high Mg coating particularly. Blank loss is small in Method-1 and considered to be effective.

Comparison of the mass loss in Method-1 and Method-2 after salt spray testing is shown in **Fig. 2** and the cross sections are shown in **Fig. 3**. From the photos of the sections, a big difference in the amount of corrosion product is found; although this difference is scarcely noticed in Method-2 as found from Fig. 2. In Method-1, a significant difference is noticed. Based on this result, Method-1 is considered to be more effective than Method-2 in removing corrosion product of Al- and Mg-containing coating. Accordingly, Method-1 was applied in this study as the method to remove corrosion product.

3.2 Effect of Al

Samples of coating containing varied Al% of 1%, 3%, 6%, 8%, and 11% vs. Mg fixed at 1% were prepared and the corrosion resistance of the coating containing Mg was evaluated.

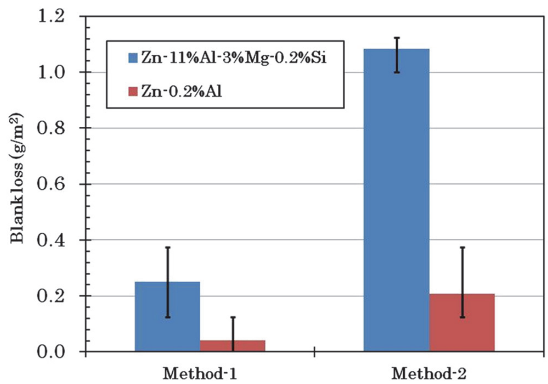


Fig. 1 Blank loss of Zn-11%Al-3%Mg-0.2%Si coating

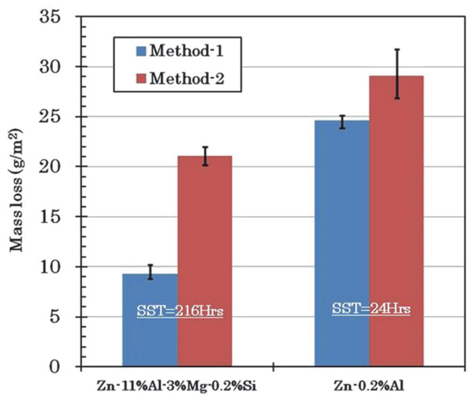
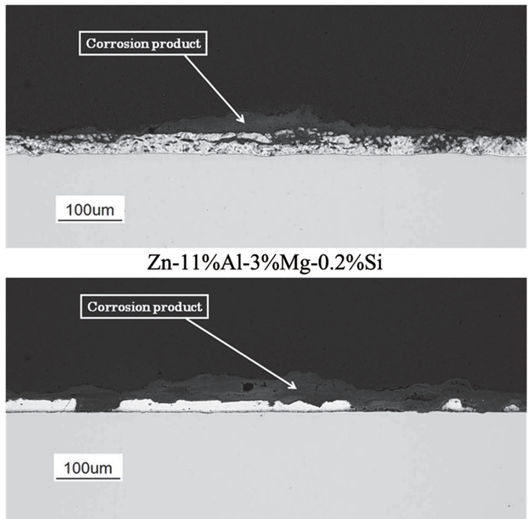


Fig. 2 Comparison of the mass loss after SST

Figure 4 shows the change of mass loss when Al% is varied. At the 15th cycle, except coating of 1% Al, no remarkable change is noticed, however, the change gradually becomes remarkable. From **Fig. 5**, wherein the number of testing cycles is taken on the horizontal axis and the corrosion mass loss (mean value of n = 3) is taken on the vertical axis, it is found that at the 15th cycle, the corrosion mass loss is almost equal except coating with 1% Al, however, at the 45th cycle, there is a significant difference in corrosion resistance between the coating with 6% Al or above and the coating with below 6% Al. In addition red rust was developed partially at 15th cycle in Zn-0.2%Al.

In the coating with 6% Al content or higher, the primary crystal is Al and this is considered to be exerting influence on the corrosion resistance in a favorable manner. From the above, improvement of



Zn-0.2%Al

Fig. 3 Cross section of the coating after SST

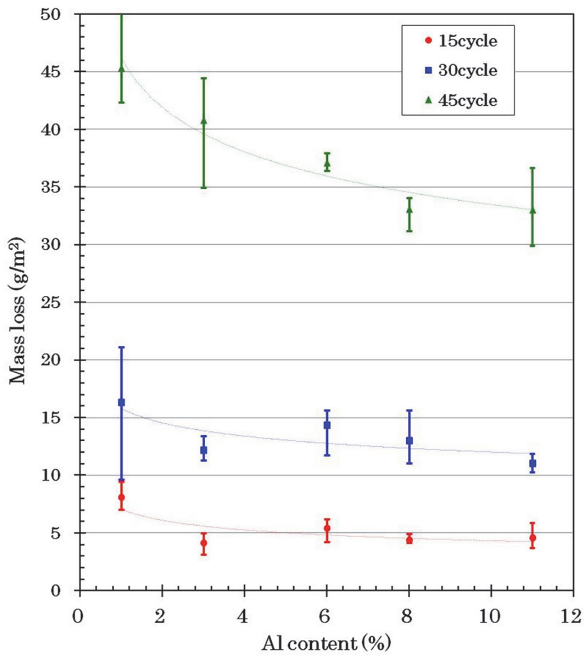


Fig. 4 Relationship between Al% and mass loss after JASO-CCT

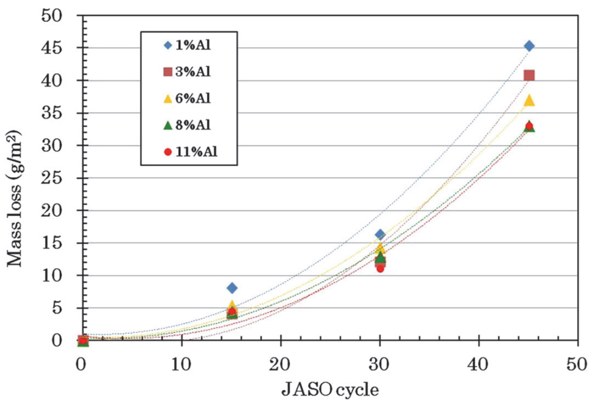


Fig. 5 Mass loss vs. JASO cycle number

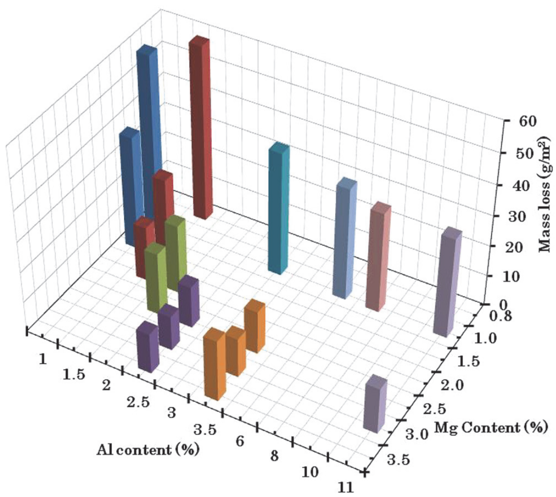


Fig. 6 Relationship among Al%, Mg% and mass loss after JASO-CCT (45th cycle)

corrosion resistance for longer duration can be expected by increasing the addition of Al.

3.3 Effect of Mg

Test samples of coating with increased addition from 1% were prepared and their corrosion resistance was evaluated with 45-cycle test of JASO-CCT. **Figure 6** shows the mass loss including the case of Mg = 1%. It is confirmed that mass loss is greatly reduced by increasing Mg% and there is improvement in corrosion resistance. The effect of increase in Al% is smaller than its effect when Mg = 1%, and difference in change is not noticeable at about 45th cycle, however, when the test proceeds to 90 cycles, coating with low Al% develops red rust (**Fig. 7**). Likewise the result of coating with 1% Mg, it is found that increase of Al% improves the long duration corrosion resistance. From this fact, addition of Al by 6%–8% or above and addition of Mg by about 3% can enhance the corrosion resistance of coating.

Furthermore, with Al% of 2.5% and 3.5%, amount of mass loss is increased when Mg% is increased from 2.5% to 3.5%, and it is found that corrosion resistance deteriorates. In this region, along with the increase of Mg%, the primary crystal changes from Zn to $MgZn_2$ (**Fig. 8**) and this is presumed to be one of the reasons.

3.4 Analysis of corrosion product

Figure 9 shows the result of XRD after the JASO-CCT corrosion test of coatings with varied Al% vs. 1%Mg. The corrosion product was mainly consisting of $Zn_5(OH)_8Cl_2 \cdot H_2O$ and it is found that no significant difference lies among the corrosion product. The result at the 90th cycle is shown in **Fig. 10**. At 3% Al or above, generation of $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ is observed.

In either case, existence of Mg-containing corrosion product was not confirmed, and the mechanism of Mg contributing to enhance the corrosion resistance could not be confirmed either.

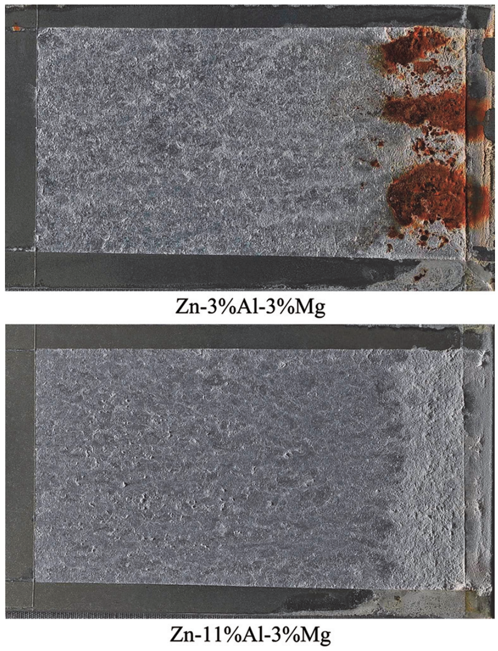


Fig. 7 Appearance after JASO-CCT (90th cycle)

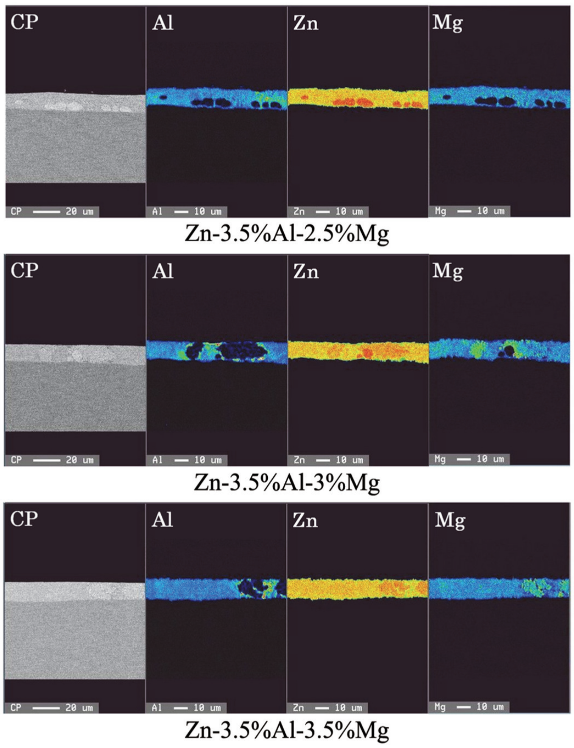


Fig. 8 EPMA data of Zn and $MgZn_2$ primary phase

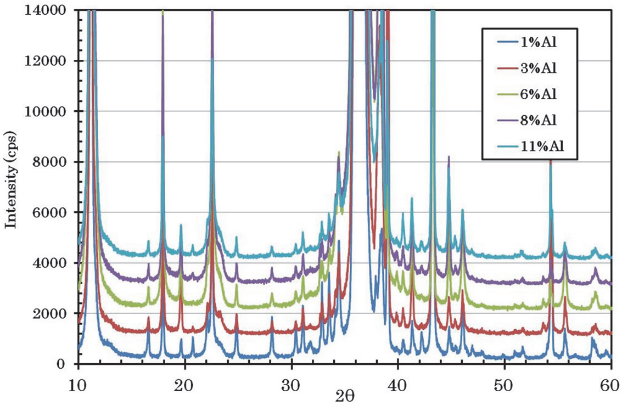


Fig. 9 XRD after the JASO-CCT of 1% Mg coating

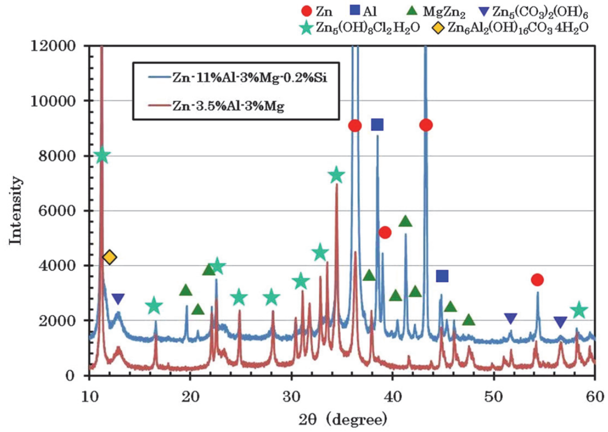


Fig. 10 XRD data after JASO-CCT (90th cycle)

4. Conclusion

(1) As the method of separating corrosion product, using ammonium dichromate was confirmed as appropriate for coating of Zn-Al-Mg system.

(2) Along with the increase of Al%, corrosion resistance is improved, and the effect of added Al becomes clear when the test is longer.

(3) Addition of Mg has greater effect than addition of Al. However, under a fixed Mg%, the higher the Al% is, the higher the corrosion resistance becomes, and it was found that addition of Al by 6–8% or above and of Mg by 3% is most appropriate.

(4) There is a possibility that corrosion resistance deteriorates when the primary crystal changes from Zn to $MgZn_2$.

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