

Highly Corrosion-resistant Zn-Mg Alloy Galvanized Steel Sheet for Building Construction Materials

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Abstract

The microstructure and corrosion product structure characteristics of the coating of highly corrosion-resistant Zn-Mg alloy galvanized steel sheet, designated "Dymazinc" and developed to prolong the service life of civil engineering and building construction materials, are described. Magnesium is abundantly distributed near dendrites in the coating and forms a Zn-Mg intermetallic compound. This is the reason that the Zn-Mg alloy coating is harder than galvanized steel and provides superior sliding performance. The corrosion products of the Zn-Mg alloy coated steel are structurally denser than the galvanized steel and mainly inhibit the cathode reaction among the corrosion reactions. Coupled with the behavior of magnesium, the corrosion products are considered to be responsible for the high corrosion resistance of the Zn-Mg alloy galvanized steel sheet "Dymazinc".

1. Preface

Hot dip galvanized steel sheets are widely used for civil and building construction applications. Demands for highly corrosion-resistant coated sheets for longer service life are expected to grow in view of increased concern over protection of global environment and conservation of resources.

As was reported previously¹⁾, Nippon Steel developed a Zn-Mg alloy galvanized steel sheet product "Dymazinc" as a highly corrosion-resistant coated sheet product for extended service life. The product having Mg as an alloying element of the coating layer is environment-friendly besides having excellent performance.

The present report describes factors of the excellent corrosion resistance of the developed product, i.e. characteristics of the coating layer structure and corrosion product for the purpose of clarifying how the corrosion resistance performance of the Zn-Mg alloy hot dip galvanized sheet product (Zn-Mg coated sheet) is brought about.

2. Test Procedures

2.1 Galvanized sheet specimens

Zn-Mg coated sheets (Mg: 0.5% - varying from 0 to 3% in some specimens; Al: 0.2%; coating weight 60 and 135 g/m²) prepared by a laboratory hot dip galvanizing simulator were used for the tests described hereafter. Zn hot dip galvanized sheets (Al: 0.2%) without Mg prepared by the same simulator were used for comparison. The conventional Al-killed low carbon, hot rolled steel sheet (SPHC under JIS) was used as the base metal.

2.2 Structural analysis of coating layer

For structural analysis of the coating layer the surface and the cross section were examined by optical microscope and SEM-EPMA. Thin samples were prepared by the ion milling method for examination of microstructure by TEM.

2.3 Analysis of corrosion behavior

Corrosion product after cyclic corrosion test (CCT: salt spray - drying - wetting - drying) or atmospheric exposure test was analyzed by X-ray diffraction method and SEM-EPMA. Electrochemical measurements such as corrosion potential measurement and polarization

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measurement of the corrosion product were also employed.

3. Test Results and Discussion

3.1 Characteristics and microstructure of Zn-Mg alloy coating layer

The surface of Zn-Mg alloy coated sheets presents a whitish dull appearance when Mg content is 0.5% or more. As shown in Fig. 1 surface hardness of the Zn-Mg coating layer is higher than that of the Zn coating layer. When Mg content exceeds 0.5% the increase in the surface hardness of the coating layer gradually comes to a saturating point. For clarifying the reason why the surface hardness of the Zn-Mg coating was higher than that of the conventional Zn coating, microstructures of the surface and cross section of the coating layer were studied. Dendrite crystals were observed in the surface of the Zn-Mg coating and the crystal grain size tended to be smaller as the Mg content in the coating layer increased.

Fig. 2 shows SEM-EPMA analysis result of the Zn-Mg coating surface (Mg: 0.5%, Al: 0.2%). From this it is apparent that Mg at the Zn-Mg coating surface is distributed mainly near the dendroid portions of the dendrite crystal. It was also observed that the area where Mg was distributed tended to be larger as Mg content increased. This is suspected to be caused by precipitation of Mg ousted out of the Zn crystal grains during solidification since, according to the Zn-Mg binary alloy phase diagram proposed by Massalaski et al.²⁾, solid solution limit of Mg in the Zn-Mg system is low (less than 0.1%) in the room temperature range.

Further, for clarifying the microstructure of Zn-Mg in the vicinity of the dendroid portions, thin film samples of the coating layer were prepared from the surface to the inside by the ion milling method. Their TEM observation revealed that Zn-Mg near the dendroids existed in the form of intermetallic compounds, $MgZn_2$ and, partially, Mg_2Zn_{11} ³⁾. This microstructure with the intermetallic compound for-

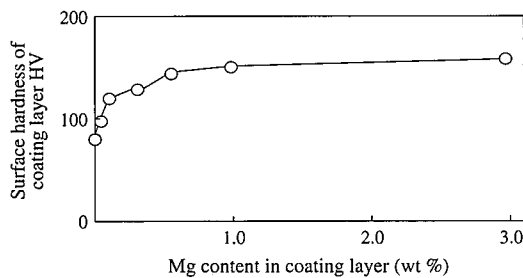


Fig. 1 Surface hardness of Zn-Mg coating layer

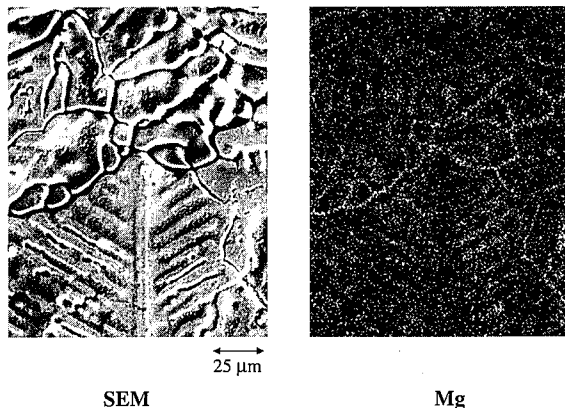


Fig. 2 Surface morphology and Mg distribution of Zn-Mg coating layer

mation near the dendrite crystal is presumed to account for the higher surface hardness of the Zn-Mg layer than the Zn layer without Mg.

3.2 Corrosion resistance behavior of Zn-Mg alloy layer

The Zn-Mg alloy coated sheet exhibits, as reported previously^{1,4)}, remarkably high corrosion resistance in environments with high salt content such as those of cyclic corrosion test and atmospheric exposure test with salt spray. It is also known that the Zn-Mg coating has a superior corrosion resistance under atmospheric exposure conditions with small salt content, although not so remarkable as in the salt-rich conditions. Behavior of corrosion product of the Zn-Mg coated sheet was investigated for the purpose of studying corrosion resistance mechanism of the product.

3.2.1 Structure of corrosion product of Zn-Mg coated sheet

Fig. 3 shows how long it took for galvanized sheets with different Mg contents in the coating layer to form red rust under cyclic corrosion tests. Resistance against red rust is improved as the Mg content becomes higher.

Fig. 4 shows differences in surface morphology and chemical composition of corrosion products of the Zn-Mg coated sheets (Mg: 0.5%, Al: 0.2%) and the Zn coated sheets without Mg (Al: 0.2%) at an initial stage of corrosion (96 h). The corrosion product of the Zn-Mg coating is more densely packed than that of the Zn coating. In terms of chemical composition, the corrosion product of the Zn-Mg coating contains higher percentage of Cl than the Zn coating, while with O the comparison is the other way around. As a result of X-ray diffraction analysis, the corrosion product of the Zn-Mg coating was confirmed to have a higher content of basic zinc chloride $ZnCl_2 \cdot 4Zn(OH)_2$ ((100) plane) and smaller content of zinc oxide ZnO ((021) plane) than the Zn coating³⁾.

Next, Fig. 5 shows X-ray diffraction of corrosion products of the Zn-Mg and the Zn coating layers after 10 months of salt spray-atmospheric exposure test once salt spray per day. The peak of zinc is far higher in the case of the Zn-Mg coating than the Zn coating without Mg, which fact means that residual coating weight of the Zn-Mg coating is much greater than the Zn coating. Also, X-ray peak intensity of zinc corrosion products of the Zn-Mg coating is generally higher than the Zn coating without Mg, showing that the residual weight of the zinc corrosion products of the Zn-Mg coating is also higher than Zn coating. Further, (as described previously) in the corrosion product of the Zn-Mg coating the content of basic zinc chloride is high and that of zinc oxide is low. In contrast to this, X-ray peak intensity of zinc corrosion products of the conventional Zn coating is low, which agrees well with the fact that the specimens were mostly covered with red rust. Little metal zinc remained in the coating layer and residual white rust was largely composed of ZnO .

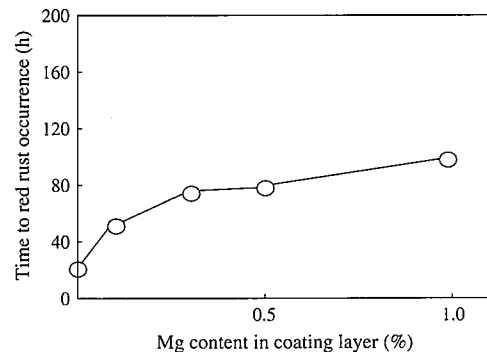
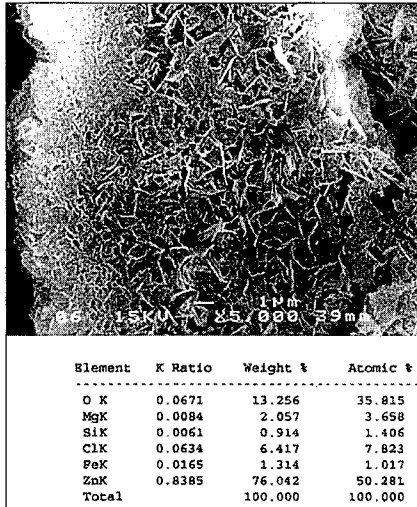
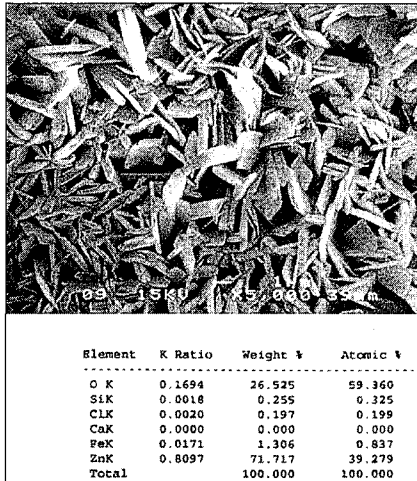


Fig. 3 Corrosion resistance of Zn-Mg coated sheet in bear use (Al: 0.2%, 60 g/m², CCT)



Zn-0.5%Mg-0.2%Al



Zn-0.2%Al

Fig. 4 Surface morphology of corrosion product

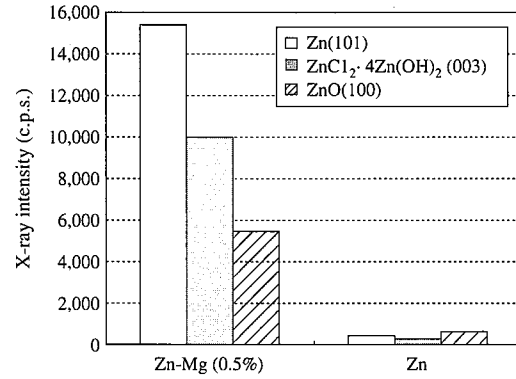


Fig. 5 X-ray diffraction of corrosion product (10 months of salt spray-atmospheric exposure test)

From these results it was confirmed that the zinc corrosion product of the Zn-Mg coating was very densely packed and that the addition of Mg made basic zinc chloride, a component of the zinc corrosion product, last stably for a long period, as had been presumed from the tests using artificial rust⁵⁾. This mechanism is considered to be one of the factors of the high corrosion resistance of the Zn-Mg coating.

Fig. 6 shows results of SEM analysis at a sectional plane of the corrosion product and CMA analysis of its element distribution of the Zn-Mg coating after the salt spray-atmospheric exposure test. Paying attention to the distribution of Cl and O, it can be observed that there is much basic zinc chloride remaining beneath the ZnO layer near the surface of the Zn-Mg coating. It can also be observed that Mg is concentrated near the surface, since it is little seen in the lower (basic zinc chloride) portion but much of it is seen in the surface (ZnO) portion. It is also possible that elution of Mg has precipitated in the form of hydroxide in the surface portion⁶⁾.

3.2.3 Polarization behavior of corrosion product

Fig. 7 shows change of corrosion potential of the Zn-Mg coated sheet immersed in 0.03% and 3% salt water. Corrosion potential of the new product was nearly the same in either of the salt concentrations and it was pretty similar to that of the conventional product,

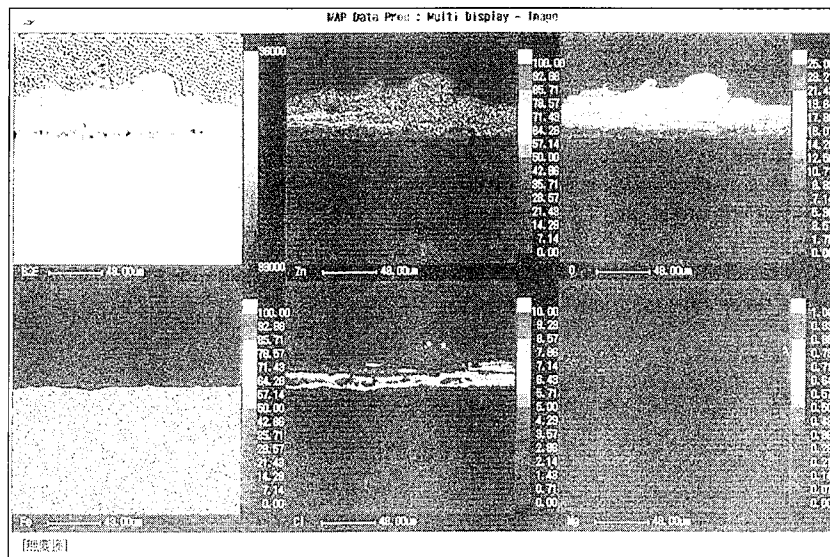


Fig. 6 Distribution of Mg in corrosion product

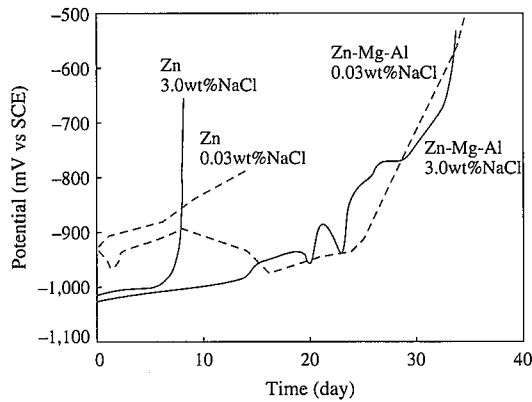


Fig. 7 Time dependence of corrosion potential

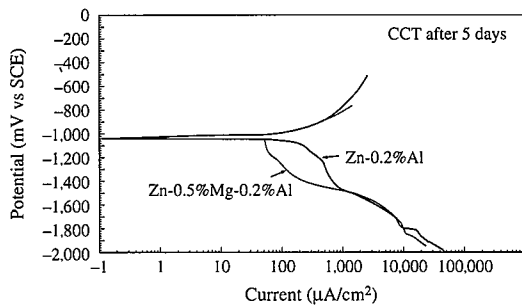


Fig. 8 Polarization curves of corrosion product

but the corrosion potential of zinc is kept for a longer time in the case of the Zn-Mg coating than the Zn coating. This agrees well with the fact that zinc corrosion product of the Zn-Mg coating is maintained stably for a long period in the corrosion tests. It means that sacrificial corrosion protection effect of zinc is kept for a long time in the Zn-Mg coated product.

Fig. 8 shows polarization curves of zinc corrosion product at an initial stage of corrosion³⁾. The Zn-Mg coating had lower limited diffusion current of cathodic reaction (oxygen reduction reaction) than the Zn coating. This is probably because the densely packed corrosion product of the Zn-Mg coating is hindering the diffusion of oxygen and this fact seems to be one of the main reasons for the high corrosion resistance of the developed product. With regards to anodic reaction, both the Zn-Mg coating and the Zn coating were nearly the same but, considering the fact that the corrosion product of the Zn-Mg coating is kept stable in a thin layer and much of Mg is observed near the upper layer of the corrosion product, it is possible that the Mg in the corrosion product is contributing to the reaction as small anodes.

From the results of the above test it is suggested that the characteristic close-packed structure of the corrosion product and the be-

havior of Mg in it are related to the high corrosion resistance of the Zn-Mg coating.

4. Summary

The following observations were obtained from the investigations of microstructure and corrosion behavior of the coating layer of the new high corrosion resistant Zn-Mg alloy galvanized sheet “Dymazinc” developed for civil and building construction applications:

- 1) Mg in the Zn-Mg alloy coating layer is distributed mainly in the vicinity of dendroid portion of dendrite crystal.
- 2) Zn-Mg in the dendrite crystal of the coating layer was found by TEM to exist in the form of $MgZn_2$ or, partially, Mg_2Zn_{11} . This fact is suspected to be the reason for the product’s characteristic high hardness and good sliding property of the coating layer.
- 3) Corrosion product of the Zn-Mg coating is composed of more basic zinc chloride than ZnO and is far more densely packed than the same of the Zn coating without Mg.
- 4) Under a corrosion test in a highly chloric atmosphere Mg in the corrosion product of the Zn-Mg coating was found to concentrate in the upper ZnO layer and little existent in the lower thin layer of basic zinc chloride.
- 5) Corrosion potential of the Zn-Mg coating is similar to that of the Zn coating but the potential of zinc is maintained for a longer period than the Zn coating. Regarding polarization behavior of corrosion product, cathodic reaction, among corrosion reactions, of the Zn-Mg coating is remarkably lower than that of the Zn coating.
- 6) It was suggested that the peculiar form of corrosion product of the Zn-Mg coating and behavior of Mg in it were contributing to the high corrosion resistance of the product.

5. Conclusion

The newly developed Zn-Mg coated sheet “Dymazinc” having high corrosion resistance can offer a long service life of fabricated products and is expected to contribute significantly to environmental protection and conservation of global resources. Besides substituting post-galvanizing of steel structures for civil and building constructions, it is also promising as a replacing material for concrete and wood.

References

- 1) Shindo, H., Nishimura, K., Okada, T., Nishimura, N., Asai, K.: Shinnittetsu Giho. (369), 61 (1998)
- 2) Massalski, B. T. et al.: Binary Alloy Phase Diagrams. 2nd ed. 1986, p.2572
- 3) Nishimura, K. et al.: Proc. GALVATECH98, 437 (1998)
- 4) Shindo, H., Nishimura, K.: CAMP-ISIJ. 9, 1277 (1996)
- 5) Okada, H., Yamamoto, K., Ito, I.: Proc. International Congress on Metallic Corrosion, 275 (1972)
- 6) Pourbaix, M.: Atlas of Electrochemical Equilibria in Aqueous Solutions. London, New York, Pergamon Press, 1996