NIPPON STEEL TECHNICAL REPORT No. 87 JANUARY 2003

UDC 669 . 586 : 669 . 55' 71' 721' 282 : 669 . 14 - 416

Excellent Corrosion-resistant Zn-Al-Mg-Si Alloy Hot-dip Galvanized Steel Sheet "SUPER DYMA"

Yasuhide MORIMOTO*1 Kazuhiko HONDA*1
Kazumi NISHIMURA*1 Satoru TANAKA*1
Akira TAKAHASHI*1 Hidetoshi SHINDO*1
Masao KUROSAKI*1

Abstract

For the improvement in corrosion resistance of Zn-5%Al hot-dip galvanized steel sheet, "SUPER DYMA" (excellent corrosion-resistant Zn-Al-Mg-Si alloy hot-dip galvanized coating) was developed. It was found that the increase of Al, Mg content in coating and the addition of Si improved corrosion resistance of the coating in salt spray tests. The polarization in 5% NaCl solution is considered to be the factor of high corrosion resistance in that the anode and the cathode reaction are inhibited compared with Zn-5%Al coating. Moreover, the edge-creep nature after the cyclic corrosion test on painted samples and the corrosion resistance in an outdoor exposure environment of "SUPER DYMA" are also superior to Zn-5%Al galvanized steel sheet.

1. Introduction

As a variety of hot-dip galvanized steel sheet products for construction use, a steel sheet product plated with a Zn-5%Al series alloy has been widely applied in virtue of its high corrosion resistance with a comparatively small coating weight[1-3]. In fact, its corrosion resistance of plating at a salt spray test is twice as high as that of a conventional hot-dip Zn-plated sheet product.

Lately, however, demands for plated sheet products having even better corrosion resistance are increasing in view of the requirements for a very long service life, enhanced performance, etc. in housing and other buildings. Nippon Steel Corporation studied hot-dip Zn-alloy-plated steel sheet products aiming at further enhancing the corrosion resistance of hot-dip galvanized steel sheet products for construction use and as a result, has developed a highly corrosion resistant hot-dip galvanized steel sheet "SUPER DYMA" (a steel sheet plated with Zn-11%Al-3%Mg-0.2%Si alloy). This paper reports on the effects of the component elements of the plating alloy on corrosion resistance and the corrosion resistance of the new product.

2. Experimental

Most of the galvanized steel sheets used for the tests were produced on a batch type galvanizing simulator for laboratory use (Rhesca make). Material sheets of a low carbon Al-killed steel were heated to 800°C in an N_2 atmosphere containing 10 volume % of H_2, held at the temperature for 60 s, cooled with N_2 gas to 500°C, then dipped in a Zn alloy plating bath at 450°C for 3 s, and cooled to the room temperature after controlling the coating weight by N_2 gas wiping.

The composition of the Zn alloy plating bath was changed within the following ranges: Al, from 5 to 11%; Mg, from 0 to 3%; and Si, from 0 to 0.2%. The composition of the plating layers of test pieces was analyzed by the inductive coupled plasma method (ICP) after dissolving them using hydrochloric acid.

The corrosion resistance of plating was evaluated on plated specimens without any additional treatment through measurement of corrosion weight loss at a salt spray test in accordance with JIS Z 2371 (hereinafter SST). The corrosion resistance after painting was evalu-

*1 Technical Development Bureau

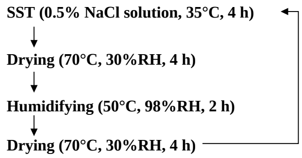

Fig. 1 Condition of cyclic corrosion test

ated in the following manner: specimens were subjected to a chromate treatment of 50 mg/m^2 in terms of Cr deposit; then, an epoxy paint 5 μm in thickness and an acrylic paint 15 μm in thickness were applied to them as a primer and a top coat, respectively; the specimens underwent a corrosion test under the cycle shown in **Fig. 1**; and the edge creep width at a cut end face was measured.

The polarization of a plating film was measured using a potentiostat (Solortron make). The specimens were immersed in a 5% NaCl solution for 3 h, using a Pt electrode as a counter electrode and an Ag/AgCl electrode as a reference electrode, and then, anode and cathode polarization was conducted at a potential scanning rate of 1 mV/s.

3. Test Results

3.1 Influences of Alloying Elements on Corrosion Resistance of Plating

Fig. 2 shows the influence of Al on the corrosion weight loss at an SST for 500 h. Here, the content of Mg in the plating alloys other than that of a Zn-5%Al-0.1%Mg alloy-plated sheet (hereinafter SZ sheet) was fixed at 3%. It is clear from the figure that when the Al content in a plating alloy is increased, corrosion weight loss decreases, evidencing an improvement in the corrosion resistance of plating.

Fig. 3 shows the influence of Mg on the corrosion weight loss of plating at an SST for 500 h. Here, the content of Al in the plating alloys other than that of the SZ sheet was fixed at 11%. It is clear from the figure that, when the Mg content in a plating alloy is increased, corrosion weight loss decreases, showing that the corrosion

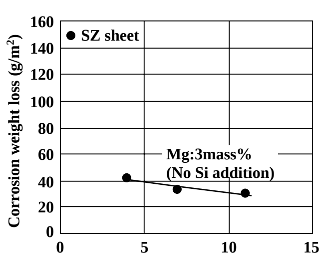

Fig. 2 Influence of Al content in plating metal on corrosion weight loss at 500-h SST

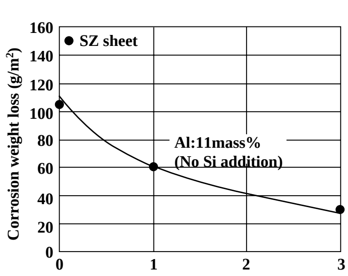

Fig. 3 Influence of Mg content in plating metal on corrosion weight loss at 500-h SST

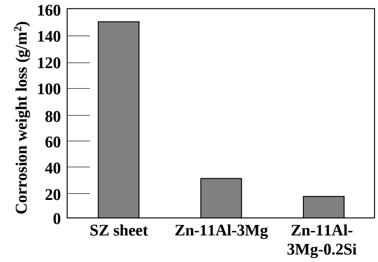

Fig. 4 Influence of Si content in plating metal on corrosion weight loss at 500-h SST

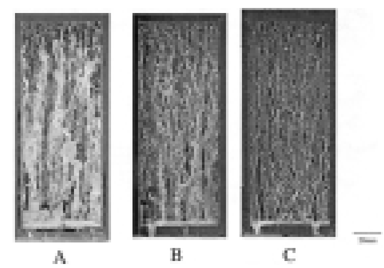

Fig. 5 Plating appearance after 500-h SST (A: SZ sheet; B: Zn-11%Al-3%Mg-plated sheet; C: Zn-11%Al-3%Mg-0.2%Si-plated sheet)

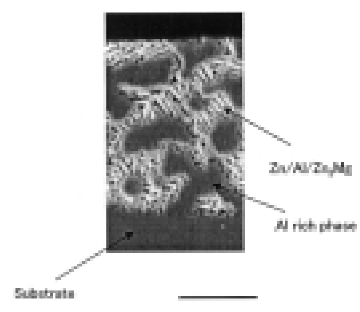

Fig. 6 Sectional micrograph of Zn-11%Al-3%Mg-0.2%Si-plated sheet

resistance of plating is improved.

Fig. 4 shows the influence of Si on the corrosion weight loss of plating at an SST for 500 h. It is seen from the figure that when a small amount of Si is added to the Zn-11%Al-3%Mg plating alloy, corrosion weight loss decreases, and thus the corrosion resistance of plating is improved yet further.

Fig. 5 shows the appearances of plating surface after an SST for 500 h. It is clear from the figure that when the contents of Al and Mg in the plating alloy of the SZ sheet are increased and Si is added to it, the occurrence of white rust is suppressed and the corrosion resistance of plating is improved. The above results show that the corrosion resistance of plating of the Zn-11%Al-3%Mg-0.2%Si alloy in a salt spray environment is remarkably enhanced compared with that of the SZ sheet.

Fig. 6 shows a sectional SEM image of a Zn-11%Al-3%Mg-0.2%Si alloy-plated steel sheet. It is seen here that the plating layer is characterized by consisting of an Al-rich phase and a ternary eutectic phase of Zn/Al/Zn$_2$Mg.

3.2 Corrosion Resistance after Painting

Fig. 7 shows the change in the edge creep of painted specimens at the cyclic corrosion test (CCT). The superiority of the Zn-11%Al-3%Mg-0.2%Si alloy-plated sheet in the corrosion resistance after painting to the SZ sheet is clear from the figure.

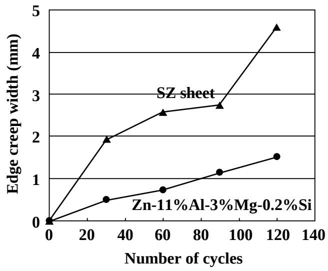

Fig. 7 Edge creep behavior at cyclic corrosion test

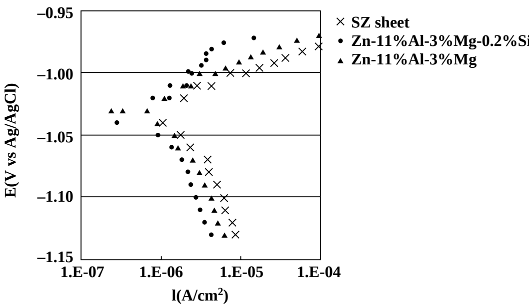

Fig. 8 Polarization after 3-h immersion in 5% NaCl solution

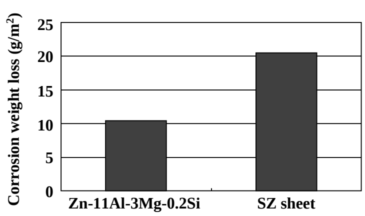

Fig. 9 Corrosion weight loss at 1-year outdoor exposure test in Okinawa

3.3 Polarization in a 5% NaCl solution

Fig. 8 shows the polarization of the plating layers of the SZ sheet and the Zn-11%Al-3%Mg and Zn-11%Al-3%Mg-0.2%Si alloy-plated sheets in a 5% NaCl solution. It is clear from the figure that, when the contents of Al and Mg in the composition of the SZ plating alloy are increased and Si is added, both the anode current and cathode current decrease. This means that both dissolution of plating, which is an anodic reaction, and reduction of oxygen, which is a cathodic reaction, are inhibited.

3.4 Plating Corrosion Behavior at Outdoor Exposure Test

Fig. 9 shows the corrosion weight losses of the SZ sheet and the Zn-11%Al-3%Mg-0.2%Si alloy-plated sheet after an outdoor exposure test for 1 year in Okinawa Prefecture. It is clear from the figure that the Zn-11%Al-3%Mg-0.2%Si alloy-plated sheet has better corrosion resistance than the SZ sheet in an outdoor exposure environment, too.

4. Summary

(1) Corrosion resistance of plating at an SST is significantly increased by adding Al and Mg to the plating alloy composition of the SZ sheet, and the corrosion resistance is increased yet further by adding Si in addition.

(2) Judging from the result of a cyclic corrosion test, the Zn-11%Al-3%Mg-0.2%Si alloy-plated steel sheet is superior in edge creep resistance after painting to the SZ sheet.

(3) Judging from the result of a polarization measurement, both the anode current and cathode current of the Zn-11%Al-3%Mg-0.2%Si alloy-plated steel sheet are lower than those of the SZ sheet, evidencing better corrosion resistance.

(4) The Zn-11%Al-3%Mg-0.2%Si alloy-plated steel sheet also shows better corrosion resistance of plating at an outdoor exposure environment than does the SZ sheet.

References

1) U.S.Patent, No.4029478
2) Tano, K., Higuchi, S.: Seitetsu Kenkyu. (315), 34 (1984)
3) Pelerin, J. et al.: Journal of the Surface Finishing Society of Japan. 33, 474 (1982)