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Chromate-free Electro-galvanized Steel Sheets for Automobile Use, “ZINKOTE-MZ”

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Abstract

Newly developed electro-galvanized steel sheet with Mg containing phosphate film (ZINKOTE-MZ) has the same or better corrosion resistance, paintability, press formability, and spot weldability compared with the conventional organic composite coated steel sheet (WU). Furthermore, MZ can be used as substitutes of WU. The effect of Mg containing phosphate film on corrosion resistance was investigated. It was suggested that the film could delay the start of Zn corrosion and also could stabilize the corrosion products of Zn.

1. Introduction

Galvannealed steel sheets and organic-composite-coated electro-galvanized steel sheets (hereinafter referred to as the WU sheets) have accounted for a good part of surface-treated steel sheets for automotive use in Japan[1]. Among these, the WU sheets display excellent anti-corrosion properties in spite of small coating weight, but because of their having chromate coating films and high cost of the Zn-Ni alloy plating their substitute product has been looked for. In view of the situation, as an environment-friendly (chromate-free) and economical (pure Zn plating) surface-treated steel sheet for automotive use capable of substituting the WU sheet, Nippon Steel Corporation has developed a steel sheet product called ZINKOTE MZ, which is an electro-galvanized steel sheet coated with special phosphate films containing Mg (see **Fig. 1**), and put it into practical application. This paper reports the properties of the product, focusing on the aspects peculiar to the application to automotive use, and the corrosion resistance effects of the Mg-containing special phosphate coating film.

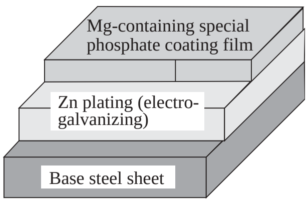

Fig. 1 Structure of ZINKOTE-MZ

2. Test Methods

2.1 Specimens

ZINKOTE-MZ steel sheets (hereinafter refereed to as the MZ sheets) produced on a commercial production line were used as specimens for the tests described below. The Zn coating weight of the MZ sheets was 30 g/m^2, and the coating weight of Zn-Ni alloy of the WU sheets that were used as comparative specimens was 20 g/m^2.

For the electro-chemical measurements and corrosion product analysis described below, specimens of the MZ sheets were prepared by forming the Mg-containing special phosphate films using laboratory facilities on the surfaces of electro-galvanized steel sheets (Zn coating weight 30 g/m^2, hereinafter referred to as the EG sheets) produced on a commercial EGL.

2.2 Evaluation of properties

2.2.1 Resistance to perforation corrosion

Boat models (models simulating the lower half of a real automobile door) were fabricated using the specimen sheets, were subjected to a cyclic corrosion test (CCT) under 50% humidity for 150 days, and the thickness loss (corrosion depth) of the steel sheets was measured at the door hemming portions of the models.

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2.2.2 Corrosion resistance after coating

Three-coat painting applied to test pieces was cross cut in X, the test pieces were subjected to a CCT under 25% humidity for 60 days, and the largest coating blister width from a cross cut line was measured.

2.2.3 Coating adhesion

Three-coat painting applied to test pieces was cross cut into 100 grids each 2 mm × 2 mm, and the area percentage of the coating remaining after peeling with an adhesive tape was measured. Evaluation was made in two stages: primary adhesion immediately after the coating and secondary adhesion after immersing the coated test pieces in warm water kept at 50°C for 10 days.

2.2.4 Coating appearance

Specimen sheets were coated by electro-deposition and the occurrence or otherwise of gas pinholes, craters, surface roughening, and so forth were observed visually.

2.2.5 Formability

Limiting drawing ratio (LDR) was measured through a cup test (punch diameter 40 mm, punch shoulder radius (Rp) 4 mm, die diameter 42.5 mm, and die shoulder radius (Rd) 8 mm) at a blank holding force (BHF) of 1 t, changing the diameter of the blanks. The maximum punch load at the time when an entire blank was brought into the die was also measured using blanks 84 mm in diameter. In this test, the antirust oil Nox Rust 550HN was used.

2.2.6 Spot-weldability

The range of optimum welding current and electrode service life (in terms of the number of consecutive spot welds of the specimen sheets to cold-rolled steel sheets) were measured using type CF-CF electrodes having a tip radius of 5 mm and at an electrode force of 1.96 kN.

2.3 Electro-chemical measurements

The polarization behaviors of the MZ sheets and the comparative EG sheets were measured using a potentio-galvanostat. Dipping potential was measured in a 5%-NaCl solution at room temperature and anodic and cathodic polarizations were done at a potential scanning rate of 0.2 mV/s; here, a platinum electrode was used as the counter electrode and an Ag/AgCl electrode as the reference electrode. The test pieces that underwent a CCT (84% humidity for 1 cycle = 1 day) for accelerating corrosion were also subjected to the same measurements.

2.4 Corrosion product analysis

The peak X-ray diffraction strength of the (003) plane of $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$, a corrosion product, on the surfaces of the test pieces having undergone the CCT (84% humidity for 1 cycle = 1 day) was measured by X-ray diffractometry using a Cu-kα ray at 40 kV, 1,200 mA.

3. Test Results

3.1 Evaluation of properties required for automotive use

The results of the above measurements of the MZ and WU sheets are summarized in **Table 1**. The performance of the MZ sheets was the same as that of the WU sheets in any of the evaluation items.

The evaluation results of the resistance to perforation corrosion are shown in **Fig. 2**. In spite of the long period of the CCT, no perforation corrosion was observed in either of the MZ and WU sheets and thus excellent corrosion resistance was confirmed. The good resistance of the MZ sheets to perforation corrosion is presumably due to the effect of the Mg-containing special phosphate coating films, which is explained later in more detail. With respect to the corrosion resistance after paint coating, as seen in Table 1, the paint blistering of the MZ sheets was equal to or even better than that of the WU sheets in terms of blister width. This is presumably because the Zn coating weight of the MZ sheets was larger than that of the WU sheets, 30 versus 20 g/m^2.

The adhesion and appearance of paint coating of the MZ sheets were also good as seen in Table 1.

Fig. 3 shows the evaluation results of formability in the cup test: the MZ sheets displayed the same values of both the LDR and maximum punch load as the WU sheets did. The same test was carried out on specimens of the EG sheets (Zn 30 g/m^2) of the same steel but without the special phosphate films (not shown in the figure), and they displayed significantly poorer values: an LDR of 2.15 and a maximum punch load of 2.0. This indicates that the good workability realized with the MZ sheets is due to the solid lubrication effect of the Mg-containing special phosphate films formed on the surfaces of the EG sheets used as the base material.

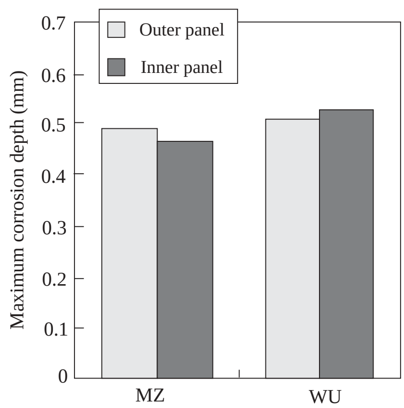

Fig. 2 Evaluation of resistance to perforation corrosion

Table 1 Comparison of properties

	Corrosion resistance		Paint adhesiveness		Coating appearance	Workability	Weldability
	To perforation corrosion	After paint coating	Primary	Secondary			
MZ	Good (Fig. 2)	Good (1.9 mm)	Good (peeling 0%)	Good (peeling 0%)	Good	Good (Fig. 3)	Good (Table 2)
WU	Good (Fig. 2)	Good (2.4 mm)	Good (peeling 0%)	Good (peeling 0%)	Good	Good (Fig. 3)	Good (Table 2)

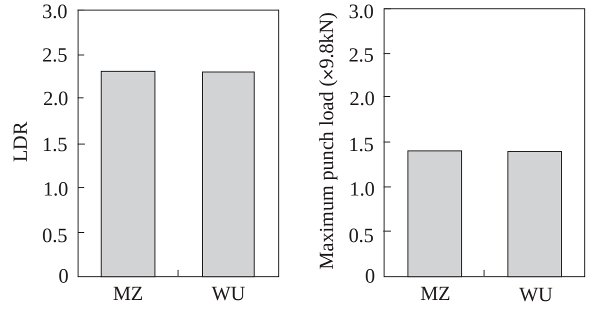

Fig. 3 Evaluation of LDR and maximum punch load

Table 2 Evaluation of spot-weldability

	Optimum welding current range			Consecutive spot welds
	I_{min} (kA)	I_{max} (kA)	Range (kA)	
MZ	8.2	9.6	1.4	More than 1,000
WU	7.6	9.0	1.4	More than 1,000

Table 2 shows the results of the spot-weldability test. The MZ sheets showed a range of optimum welding current as wide as that of the WU sheets and a long electrode service life in terms of the number of consecutive spot welds. This indicates that the phosphate coating films of the MZ sheets effectively inhibit the alloying of Cu in the electrodes and Zn in the plating layers, and the damage of electrodes resulting from it.

3.2 Electro-chemical measurements and corrosion product analysis

As explained earlier, the MZ sheets have excellent resistance to perforation corrosion. For examining the mechanism of this, the electro-chemical measurements and corrosion product analysis were carried out.

Figs. 4 and **5** show the polarization behaviors of the MZ and EG sheets before and after 2 cycles of the CCT. It can be seen in Fig. 4 that the dipping potential of the EG sheets before the CCT is equivalent to the potential of Zn (roughly –1 V), but it shifts to the nobler side after 2 cycles of the CCT, evidencing that the sacrificial corrosion protection effect of Zn has disappeared. With the MZ sheets, on the other hand, as seen in Fig. 5, the dipping potential is substantially the same before and after the CCT. With respect to the cathodic current density before the CCT, the value of the MZ sheets was lower than that of the EG sheets roughly by one order of magnitude. This indicates that oxygen reduction reactions, which are cathodic reactions, are suppressed in the MZ sheets. Looking at the change of the cathodic current density after 2 cycles of the CCT, the cathodic current density of the MZ sheets is lower than that before the CCT, again, by roughly one order of magnitude, suggesting a probability of such kinds of corrosion products as to inhibit the oxygen reduction reactions having formed at the initial stages of corrosion. As a conclusion, it is presumed that the special phosphate coating films of the MZ sheets, either in their initial state or after corrosion, inhibit the oxygen reduction reactions, contributing to the high corrosion resistance of the product.

Fig. 6 shows the change with the CCT cycles of the XRD peak strength of basic zinc chloride ($ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$) formed on the MZ and EG sheets. Whereas in the EG sheets the basic zinc

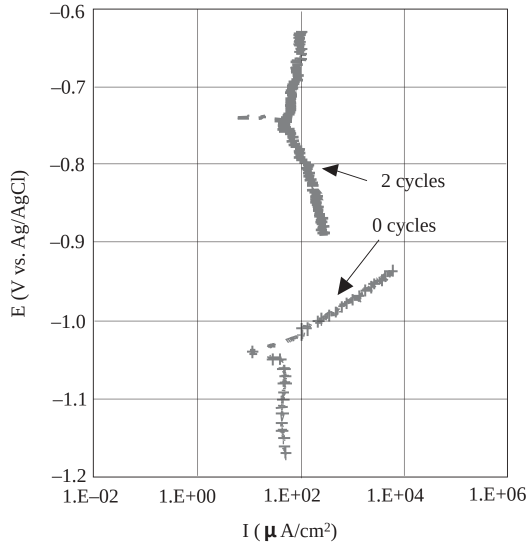

Fig. 4 Polarization behavior of EG sheets(before and after 2 cycles of CCT)

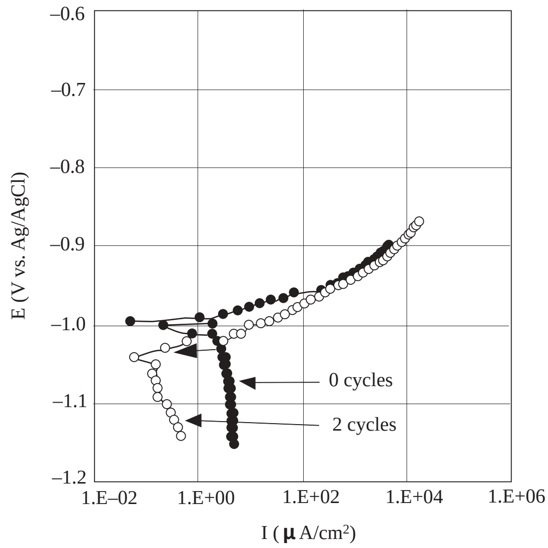

Fig. 5 Polarization behavior of MZ sheets(before and after 2 cycles of CCT)

chloride is observed from the initial stage (2 cycles) of the CCT but it decreases rapidly as the CCT cycles advance and disappears totally after 20 cycles, in the MZ sheets it begins to increase somewhere around the fourth cycle (which seems to indicate that the very corrosion of Zn little occurred earlier) and keeps a high XRD strength yet at the 26th cycle and thereafter.

Among various corrosion products of zinc, the basic zinc chloride has been considered to have a strong protective effect[2]. In addition, as a result of an experiment for investigating the transformation behavior of rust into zinc oxide under a dry condition wherein artificial rust of zinc hydroxide was used with additions of different metals, it was reported that zinc hydroxide was stabilized and its transformation into zinc oxide was inhibited when Mg was added[2]. It is presumed from this that the Mg-containing phosphate coating films of the MZ sheets partially dissolves in a corrosive environment, Mg

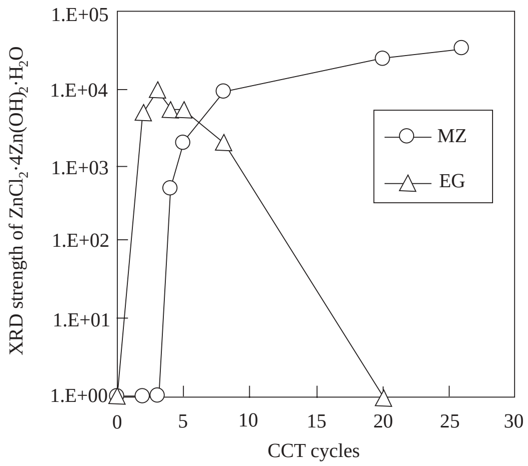

Fig. 6 Change of XRD peak strength of basic zinc chloride with progress of corrosion

is absorbed in corrosion products and as a consequence, stabilizes basic zinc chloride, which exhibits a strong protective effect, and that this is another reason for the high corrosion resistance of the MZ sheets.

4. Conclusion

Newly developed ZINKOTE-MZ shows corrosion resistance, paintability, workability and spot-weldability as good as those of the WU product conventionally used. It can replace the WU product without problem. Actually, the replacement is already taking place. The excellent properties of the new product described above are realized owing largely to the effects of the newly developed Mg-containing special phosphate coating film.

Reference

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