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THE EFFECT OF Mg CONCENTRATION AND LAYER THICKNESS ON THE ADHESION OF ZnMg-Zn BI-LAYERED PVD COATINGS

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ABSTRACT

For many years zinc coatings have been regarded as one of the most effective corrosion protective coatings for steel. Recently, it has been shown that the addition of even small amounts of magnesium to the zinc coating can noticeably increase its corrosion protection performance. However, poor adhesion of ZnMg coatings to advanced high-strength steels is observed. The addition of a more ductile Zn interlayer between the steel substrate and ZnMg coating is a solution to improve the adhesion. In the present study, a series of ZnMg-Zn bi-layered coatings with different Mg concentrations (up to 14.1 wt.% Mg) and also different thicknesses of the Zn and ZnMg layers were prepared by a thermal evaporation process to investigate the adhesion performance/interfacial adhesion strength. The adhesion performance of the coatings was qualified by the BMW crash adhesion test (BMW AA-M223), while the interfacial adhesion strength at the ZnMg/Zn interface was quantified by scratch test. It is found that the interfacial adhesion strength decreases gradually with increasing the Mg content of the top layer. The novel finding is that the interfacial adhesion strength at the ZnMg/Zn interface is independent of the thickness of the Zn interlayer. However, the adhesion performance of a ZnMg-Zn bi-layered coating during bending test is a complex function of different parameters such as the thickness of Zn and ZnMg layers, interfacial adhesion strength and interfacial defects density.

Keywords: ZnMg-Zn bi-layered coating; Physical vapor deposition (PVD); Adhesion, Scratch test

1 INTRODUCTION

For many years, Zn coatings have been known as one of the most effective corrosion protective coatings for steel [1]. Recently, it has been shown that the addition of alloying elements such as Ni [2], Cr [3], Al [4] and Mg [5] to the pure zinc increases its corrosion protection performance, considerably. The advantage of Mg over other elements can be described by its effectiveness even in the low alloying concentration [6]. Higher corrosion resistance of ZnMg coatings compared to the pure zinc is related to the formation of a dense protective layer called "simonkolleite" by the addition of magnesium which acts as a barrier to the corrosive media [7]. Different methods are commonly used to deposit pure or alloyed zinc coatings on steel substrates such as hot-dip galvanizing (HDG) and electrodeposition [8]. However, some drawbacks such as inability of producing highly alloyed ZnMg coatings, depositing multilayered coatings, hydrogen embrittlement (specially for advanced high strength steels), high temperature impact on the steel, high costs and environmental impact can limit their applicability. Physical vapor deposition (PVD) can be considered as a favorable technique to replace the conventional methods as it can be performed at much lower substrate temperatures (~250-300 °C) and fulfills the strict environmental regulations [9].

Although the addition of Mg to the Zn is beneficial for the corrosion resistance, it reduces the adhesion of the coating to the steel substrate [10-11]. However the effect of the Mg content of the ZnMg layer and also the relation between the thickness of the Zn interlayer and of the ZnMg top layer on the adhesion of ZnMg-Zn coatings are not yet fully understood. To fill this gap, a series of ZnMg-Zn bi-layered coatings with different Mg concentrations and also different thickness of Zn and ZnMg layers are deposited on the steel substrate and evaluated by both bending and scratch tests.

2 EXPERIMENTAL

ZnMg-Zn bi-layered coatings with different Mg concentrations (0 to 14.1 wt.% Mg) and also different thickness of the Zn and ZnMg layers are deposited on a low carbon steel substrate (commonly called black plate steel) and a DP800 type of steel using thermal evaporation process. The chemical composition of the steel substrates is shown in Table 1. The vacuum chamber of the PVD machine is equipped with two crucibles containing pure Zn and a ZnMg alloy respectively. The surface of the steel strip is pretreated by a plasma magnetron based sputter unit to remove the surface oxides. The evaporators use an induction coil system to melt and thermally evaporate the Zn-ZnMg source material. The metal vapor passes through a vapor distribution box and is deposited on the surface of the running steel strip. The ZnMg top layers are labelled as ZnMgX with X indicating the Mg content in weight percent.

Table 1 Chemical composition (wt.%) of DP800 and black plate steels.

Substrate	**C**	**Si**	**Mn**	**P**	**S**	**Ni**	**Cr**	**Cu**	**Fe**
DP800	0.153	0.386	1.487	0.013	0.007	0.018	0.02	0.015	Bal.
Black plate	0.04-0.08	0.03	0.18-0.35	0.02	0.03	0.08	0.08	0.08	Bal.

Grazing angle X-ray diffraction was used to analyze the phases present in the ZnMg layer. The incidence angle was set at 2° for all of the coatings to ensure that the diffracted X-ray is only generated from the top layer in order to discard the effect of the Zn interlayer. The cross section of the samples were mounted in an epoxy resin, ground by SiC paper and finally polished to 1 µm diamond particles. The microstructure of the coatings was evaluated using scanning electron microscope (SEM, Philips XL30 ESEM). A CSM Revetest scratch tester was used to quantify the adhesion strength of ZnMg-Zn bi-layered coatings at the ZnMg/Zn interface. In this test a diamond stylus (Rockwell C indenter with the tip radius of 200 µm) is moving along the coating with a progressive increasing load. The load at which the first visible failure (observing the pure Zn layer underneath) is recognized is considered as the critical load (L_C). The maximum load and scratch length were considered as 20 N and 10 mm, respectively for all bi-layered coatings. A minimum of 5 scratches were made and the average L_C was reported for each sample. BMW crash adhesion tests (BMW AA-M223) were also carried out to study the adhesion performance of the coatings during bending load. This method is a standard adhesion test method, broadly used in industry to qualify the adhesion of galvanized coatings. Initially, a line of an adhesive (Betamate 1496V DOW Automotive Systems) at least 150 mm in length, 4-5 mm thick and at least 10 mm in width was applied to the surface of the coating. The samples were kept at 175 °C for half an hour to cure the adhesive. After cooling, the samples were quickly bent over a 90° angle. To pass the test, the adhesively bonded joint should fail in the adhesive, not in the coating/substrate interface. The BMW adhesion test was repeated 3 times for each sample. More information about this test can be found, elsewhere [12].

3 RESULTS AND DISCUSSIONS

Figure 1 shows the phase fraction of ZnMg coatings versus Mg concentration as determined by the grazing angle XRD. When the Mg content is low (< 1.5 wt.% Mg), the top layer mostly consists of pure Zn. With an increasing the Mg content, the phase fraction of the Zn decreases gradually, while the fraction of Mg_2Zn_{11} increases.. The coating is composed of a mixture of Mg_2Zn_{11} and $MgZn_2$ at Mg concentrations higher than 6 wt.%. The phase fraction of $MgZn_2$ increases with further increase of the Mg and the ZnMg top layer coating is almost fully covered with this phase at ~ 14 wt.% Mg. Figure 2 shows the cross sectional SEM micrographs of the ZnMg-Zn bi-layer coatings with different Mg concentrations. The thickness of the zinc interlayer and the ZnMg top layer for each coating is presented in Table 2. Microstructural studies also confirm the results as found by the XRD measurements.

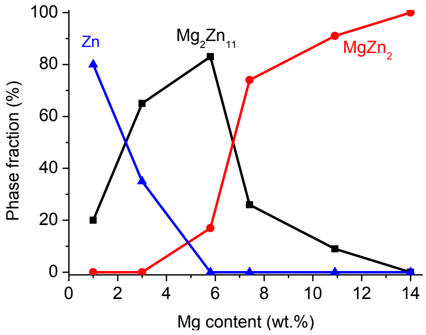

Figure 1: Phase fraction of ZnMg versus Mg content in the range of 1.5-14.1 wt.% Mg.

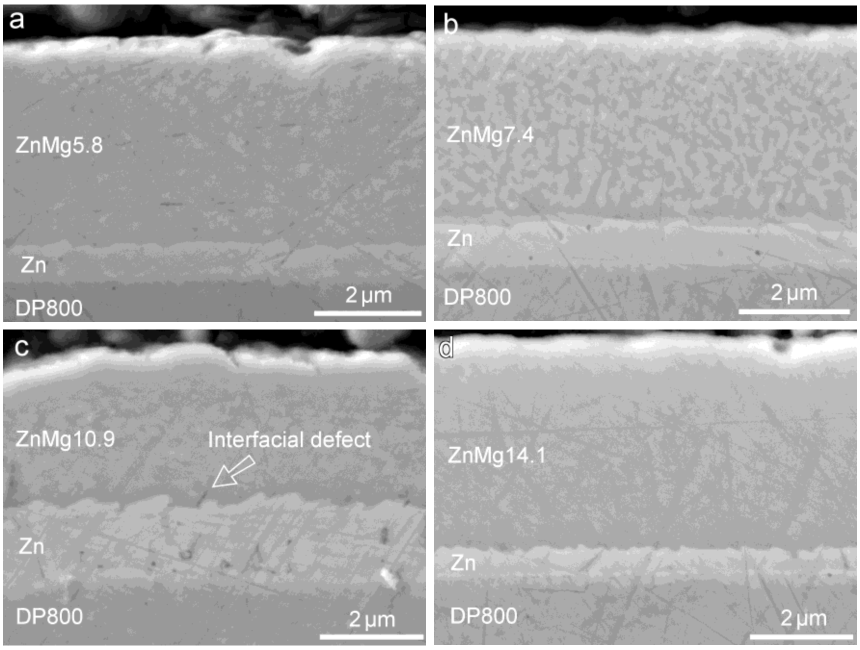

Figure 2: SEM micrographs showing the cross section of ZnMg-Zn bi-layered coatings with a ZnMg top layer of different Mg concentrations indicated.

Scratch tests were carried out to study the effect of the Mg concentration on the interfacial adhesion strength between the ZnMg and the Zn layer. Table 2 summarizes the critical load of delamination for each coating. It is worth to mention that the overall thickness of all of the coatings are in the same range. The critical load of the delamination for the pure Zn coating (38.5 N) is higher than that of all other ZnMg-Zn coatings. The L_C decreases with increasing the Mg concentration and reaches to 18.1 N and 13.2 N at 5.8 wt.% and 7.4 wt.% Mg, respectively. Further reduction of L_C is observed at even higher Mg contents. The BMW crash adhesion test revealed that all of the coatings could pass the test, except the ZnMg10.9-Zn coating. However, the L_C of this coating is still higher than that of ZnMg14.1-Zn. Therefore, it can be concluded that L_C is not a suitable criterion to compare the adhesion of different ZnMg-Zn bi-layered coatings with different Mg concentration and/or different layers thickness.

Table 2 Adhesion strength of pure Zn and ZnMg-Zn bi-layer coatings containing different Mg contents measured using scratch test.

Coating	Zn thickness (μm)	ZnMg thickness (μm)	Critical load L_C (N)	Residual depth at L_C (μm)	Weight factor ω	Adhesion strength (MPa)	BMW adhesion test
Pure zinc	4.9	0	38.5 ± 1.5	-	-	171	Pass
ZnMg5.8-Zn	0.7	3.9	18.1 ± 0.6	4.3	0.16	129	Pass
ZnMg7.4-Zn	0.9	3.7	13.2 ± 0.7	3.3	0.27	103	Pass
ZnMg10.9-Zn	1.6	3.1	9.3 ± 0.6	2.0	0.80	54	Not pass
ZnMg14.1-Zn	0.6	4.4	8 ± 0.6	1.9	0.31	78	Pass

To find a proper way for the quantification of the adhesion, the interfacial adhesion strength at the ZnMg/Zn interface was calculated by using the modified Benjamin-Weaver model [13] as follows:

$$F = \frac{K\, a\, H}{\sqrt{R^2 - a^2}} \tag{1}$$

where F is the adhesion strength (in MPa), K is constant, R is the radius of indenter tip, H is considered as the hardness of substrate and "a" is the radius of contact circle at L_C which is shown as Eq. 2.

$$a = \left(\frac{L_c}{\pi H}\right)^{0.5} \tag{2}$$

To consider the effect of both steel and zinc as the substrate for the ZnMg top layer, composite hardness was calculated using a defined weight factor as following:

$$\omega = \frac{\text{Thickness of zinc interlayer}}{\text{Residual depth at } L_C} \tag{3}$$

$$H_{composite} = \omega\, H_{Zn} + (1 - \omega)\, H_{steel} \tag{4}$$

The adhesion strength of the PVD pure Zn on steel substrate is 171 MPa, which is very comparable with the 180 MPa as reported earlier for the adhesion of hot-dipped pure Zn to the steel [14]. The adhesion strength at the ZnMg/Zn interface decreases gradually with increasing the Mg concentration and reaches to 78 MPa at 14.1 wt.% Mg. The results of the interfacial adhesion strength obtained by the scratch test follow the same trend with the results of the BMW adhesion test as the ZnMg10.9-Zn coating failed during the bending shows also the lowest adhesion strength among other samples. Such a low adhesion strength is related to the interfacial defects which are present at the interface (see Figure 2c). It is also worth to mention that the modified model can nicely reproduce the results of BMW adhesion test for the ZnMg14.1-Zn coating in contrast to only the L_C method. The ZnMg14.1-Zn coating which pass the BMW adhesion test shows higher interfacial adhesion strength compared to the ZnMg10.9-Zn coating.

The coatings containing 5-7 wt.% Mg are apparently good candidates for practical applications which requires a simultaneous good adhesion and corrosion performance of the ZnMg coatings. Therefore, to study the effect of the thickness of Zn interlayer on the adhesion, a series of coatings with the same Mg concentration (~ 6.5 wt.% Mg) and different thicknesses of the Zn interlayer (0.2, 0.7 and 1.3 µm) were prepared (Figure 3).

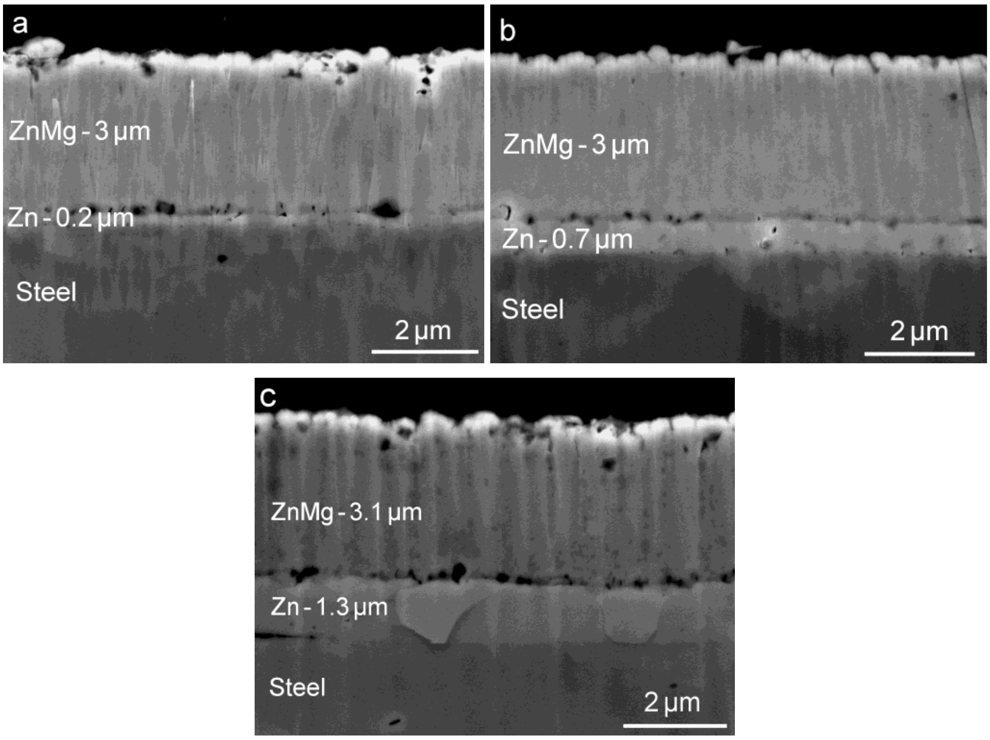

Figure 3: SEM micrographs of ZnMg6.5-Zn coatings with different thickness of the Zn interlayer.

Figure 4 shows the effect of the thickness of Zn interlayer on the L_C (Figure 4a) and the interfacial adhesion strength (Figure 4b) of the ZnMg-Zn bi-layered coatings. The L_C

increases with increasing the thickness of Zn from 11.6 to 13.25 N. However, the adhesion strength at the ZnMg/Zn interface is independent of the thickness and is around 110 MPa for the ZnMg6.5-Zn coatings. It indicates that the Mg concentration play the most dominant role on the interfacial adhesion strength rather than the thickness. It should be noted that although the interfacial adhesion strength of all these coatings is the same, the coating with the lowest thickness of the Zn failed in the BMW adhesion test, while the others passed. It can be concluded that the adhesion performance of a substrate/coating system during bending does not only depends on the interfacial adhesion strength but also to the thickness of the Zn interlayer.

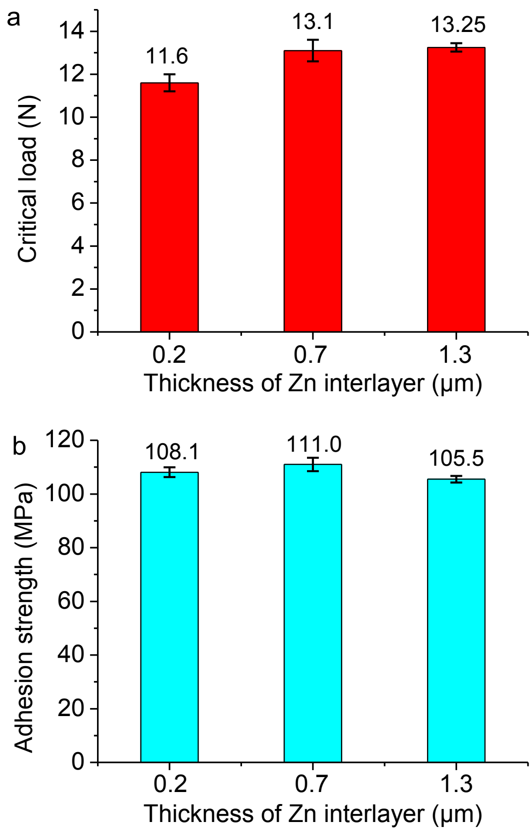

Figure 4: Critical load of delamination (a) and the interfacial adhesion strength (b) of ZnMg6.5-Zn coatings versus the thickness of the Zn.

It has been shown previously that ZnMg-Zn bi-layered coatings with a sufficient thickness of the Zn interlayer and no interfacial defects between the Zn and ZnMg layer can pass the BMW adhesion test. However, it was also observed that the thickness of ZnMg top layer can influence the adhesion performance of the coatings. The coatings fail in the BMW adhesion test when the thickness of ZnMg increases from a threshold level. Figure 5a shows the cross section SEM micrograph of a ZnMg14-Zn coating with 6.8 μm thick top layer which has failed the BMW adhesion test. The SEM micrographs of the exposed side of the coating remained on the substrate after the failure are shown in Figure 5b-d. The results of EDS analysis of different area of the failed surface are shown in Table 2. Point 1 is consisted of 95.4 wt.% Zn and 4.6 wt.% Mg, while Point 2 is consisted of 84.5 wt.% Zn and 15.3 wt.% Mg. It should be mentioned that no sign of Fe is detected on the failed surface. This results clearly indicate that ZnMg-Zn coatings with relatively thick top layer experience failure in the BMW adhesion test as the cohesive brittle failure inside the ZnMg not the adhesive failure at the interface.

Table 2 Chemical composition of different points in Figure 5b

Location	**Zn content (wt.%)**	**Mg content (wt.%)**	**Fe content (wt.%)**
Spot 1	95.4	4.6	0
Spot 2	84.7	15.3	0

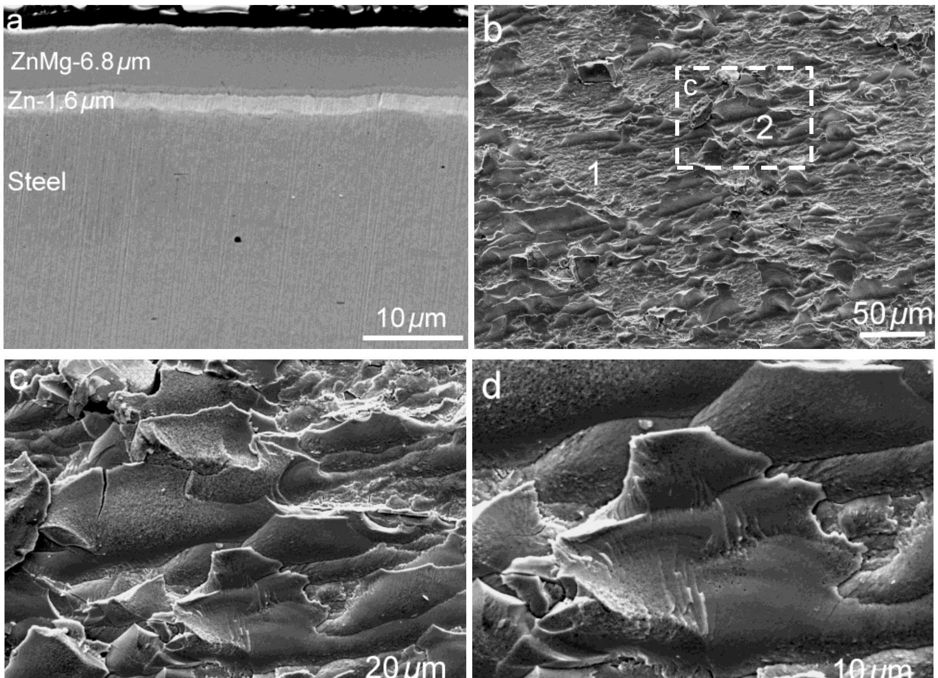

Figure 5: (a) SEM micrograph showing the cross section of ZnMg14-Zn coating containing 6.8 µm thick ZnMg top layer, (b-d) SEM micrographs of the exposed side of the coating which remains on the substrate after failure in BMW crash adhesion test.

As a summery, it can be concluded that the adhesion performance of a ZnMg-Zn bi-layered coating during bending test is a complex function of different parameters such as the thickness of both the Zn and ZnMg layer, interfacial adhesion strength and the interfacial defect density as schematically drawn in Figure 6.

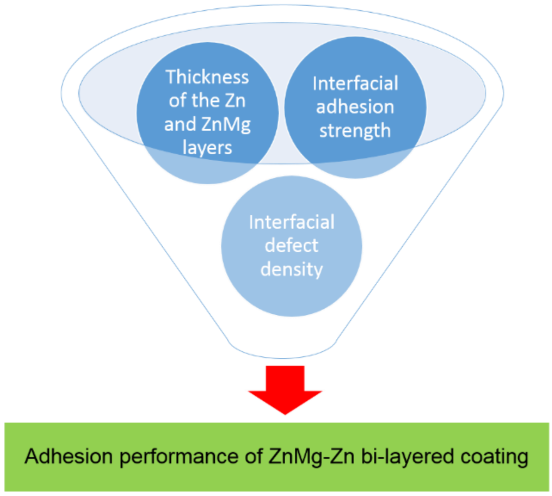

Figure 6: Parameters influencing the adhesion performance of ZnMg-Zn bi-layered coatings in the BMW crash adhesion test.

4 CONCLUSIONS

The effect of the Mg concentration and the thickness of Zn and ZnMg layers were studied on the adhesion of ZnMg-Zn bi-layered coatings by the scratch and BMW crash adhesion tests. The novel findings are summarized as following:

(1) The critical load of the delamination is not a proper criterion to compare the adhesion of the ZnMg-Zn bi-layered coatings with different composition and/or thickness ratio.

(2) Benjamin-Weaver model needs to be modified to be able to calculate the adhesion strength at the ZnMg/Zn interface by taking into account the L_C, thickness of the Zn interlayer and hardness of both substrate and interlayer.

(3) The same trend is observed between the interfacial adhesion strength calculated by the scratch test and the BMW adhesion test which is currently being used in industry for qualification of the adhesion.

(4) The adhesion strength at the ZnMg/Zn interface depends on the Mg concentration of the top layer, but not on the thickness of the Zn interlayer. The interfacial adhesion strength decreases gradually with increasing the Mg concentration.

(5) The adhesion performance of a ZnMg-Zn bi-layered coating during bending test is a complex function of different parameters such as the thickness of Zn and ZnMg layers, interfacial adhesion strength and the defect density at the interface.

ACKNOWLEDGMENTS

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