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New insight into the loss of adhesion of ZnMg-Zn bi-layered coatings on steel substrates

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Abstract

In this research, physically vapor deposited Mg-Zn and ZnMg-Zn bi-layered coatings were annealed at 180 °C for different annealing times to study the origin of the adhesion loss during heat treatment. In the case of Mg-Zn bi-layered coatings, it was observed that MgZn₂ and Mg₂Zn₁₁ intermetallics are formed during annealing from Zn and Mg by diffusion, which results in a reduction of the thickness of the initial pure zinc interlayer. In the case of ZnMg-Zn bi-layered coating, the “interfacial adhesion strength” at the ZnMg/Zn interface was quantified by using scratch test. The novel finding is that the adhesion strength of as-deposited coatings at the interface of ZnMg/Zn is independent of the thickness of the zinc interlayer (t_{Zn}). t_{Zn} decreases gradually during annealing at 180 °C. The “adhesion performance” of the studied coatings, as tested by BMW crash adhesion test (BMW AA-M223), drops drastically when t_{Zn} is less than a threshold (~ 500 nm). The obtained results indicate that t_{Zn} plays the significant role in the adhesion performance of ZnMg-Zn bi-layered coatings.

Keywords: ZnMg-Zn bi-layered coating; Adhesion strength; Annealing treatment; Thickness of Zn interlayer; Scratch test, Adhesion loss

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1 Introduction

Zinc is a well-known protective coating for steels and it acts as a sacrificial anodic layer against environmental corrosion. Zinc coated steels are mainly used in automotive industry and construction applications [1-3]. These coatings are conventionally applied by electrodeposition and hot dip galvanizing (HDG) [1-3]. In the past decades, many efforts have been made to improve the corrosion resistance of zinc coated steels by Al and/or Mg alloying. It was discovered that the addition of even a small amount of Mg (~ 1 %) can considerably enhance the corrosion performance of Zn coatings through the formation of corrosion resistant Mg_2Zn_{11} and $MgZn_2$ intermetallic compounds [4-5]. The formation of simonkolleite in the corrosion product is widely accepted as the main reason for improvement of the corrosion performance in ZnMg coatings [4-5]. Despite of the positive influence of Mg addition to the zinc coatings, new challenges arise with the production of ZnMg coatings by conventional methods. The concentration of Mg in the HDG is rather limited, and yet multilayered coatings are not possible to produce. Furthermore, dross formation and Mg burning can be mentioned as some more drawbacks of HDG for the production of highly alloyed ZnMg coatings [6]. The cost of electro-galvanizing is rather high and may also induce some environmental impacts. Physical vapor deposition (PVD) is a very interesting alternative to deposit ZnMg based coatings due to the possibility to deposit coatings with a large variety of compositions, multilayers and the low heat impact on the steel substrate. There is virtually no limitation for the chemical composition of ZnMg coatings during the PVD process and it is possible to easily adjust the Mg content to obtain maximum corrosion resistance. PVD can also fulfill strict environmental regulations as no hazardous chemicals are used as in electrodeposition. [7].

Most of the researches on ZnMg coated steels are mainly focused on the corrosion resistance and only a few studies have been published concerning the coating adhesion performance. On the other hand, degradation of coating/substrate system during post processing of ZnMg coatings (such as paint baking cycle in automotive industry) determines the lifetime and durability of the product. There are just scant publications addressing the negative influence of annealing treatment on the adhesion of ZnMg coatings on steel substrate. Byun et al. have used a OT bending test to study the effect of a short annealing time at 200 °C on the adhesion of Zn-Mg-Zn multilayer coated steel [8]. It was found that the volume fraction of the intermetallic compounds increases with the increasing of the annealing time and the adhesion drops drastically after 240 sec at which, around 90 % of the microstructure consists of the intermetallic compounds. Zoestbergen et al. [9] also indicated the negative influence of a long-time annealing at 180 °C on the adhesion of Mg-Zn bi-layered coatings, as determined by the so called “BMW crash adhesion test”. The diffusion of Mg from the top layer towards the Zn/steel interface and its segregation were reported as a possible reason for the reduced adhesion after the heat treatment.

So far, different reasons are reported for the loss of adhesion of ZnMg PVD coatings during annealing. In the present investigation, some experiments have been designed to further study the origin of the adhesion loss of the ZnMg-Zn bi-layered coatings during annealing treatment.

2 Materials and Methods

Thermal vapor deposition technique was used to deposit Mg-Zn and ZnMg-Zn coatings on two different steel substrates (see Table 1 for the chemical composition of steel substrates). The vacuum chamber of the PVD machine was equipped with two induction heated crucibles to evaporate Zn and Mg or ZnMg melts. The generated vapor flows through

the vapor distribution box (VDB) and condenses on the steel surface running above the VDB. Two Mg-Zn bi-layered coatings were prepared on black plate through the deposition of 0.5 and 0.75 μm thick pure Mg layer on a 2 μm thick pure zinc interlayer. Three ZnMg-Zn bi-layered coatings were also deposited on a DP800 steel substrate with a pure zinc interlayer of different thicknesses (0.2 μm , 0.7 μm and 1.3 μm). The thickness of the ZnMg top layer and its chemical composition were kept unchanged at $\sim 3 \mu\text{m}$ and 6.5 wt.% Mg, respectively. Table 2 summarizes the thickness of each layer for the different coatings used in this research. The samples in Table 2 are named as $\text{Zn}_x\text{-Mg}_y$ or $\text{Zn}_x\text{-ZnMg}_z$ where x, y and z indicate the thickness in micrometer of pure Zn, pure Mg and ZnMg layer, respectively. Annealing was performed in a vacuum furnace at 180 °C for different periods (up to 144 h) to study the adhesion performance of the bi-layered coatings.

Grazing angle X-ray diffraction (GAXRD) was used to identify the phases in the as-deposited and annealed samples. The incidence angle was 2° for all of the experiments to ensure that the X-ray patterns are only obtained from the ZnMg top layer. The microstructure of the coatings were studied by scanning electron microscopy (Philips XL30 ESEM) and transmission electron microscopy (JEOL 2010F) equipped with an EDS detector. The cross section of the coating samples for SEM analysis was made by an ion beam cryo cross section polisher (JEOL IB-19520CCP) at -140 °C to avoid any possible beam-generated defects.

Scratch tests were performed to quantify the “interfacial adhesion strength” of the ZnMg-Zn bi-layered coatings. A Rockwell C indenter (200 μm in radius) was used with a maximum load of 20 N for all experiments. A minimum of 5 scratches were carried out per sample. The scratch tracks were carefully investigated by SEM to find out the normal load at which delamination starts at the interface of ZnMg/Zn and the average value was reported as the critical load (L_C). Qualitative assessment of the adhesion of the coatings was also performed by the BMW crash adhesion test (BMW AA-M223) to show the “adhesion performance” of

the coating systems [9]. A coating passed the test if the bonded adhesive joint failed at the adhesive/coating interface during bending instead of in the coating or at the coating/substrate interface. Three samples were tested for each condition. Clear distinction should be made between the two terms “adhesion strength” and “adhesion performance”. The former is an intrinsic property of the interface and can be well measured by scratch test, and the latter is more extrinsic depending on the actual loading condition.

3 Results and discussion

Mg-Zn bi-layered coatings (Zn2-Mg0.5 and Zn2-Mg0.75) were annealed at 180 °C for 144 h to promote the formation of ZnMg compounds in the top layer. The BMW crash adhesion test revealed that although both samples could pass the test in the as-deposited condition, the Zn2-Mg0.75 fails after the annealing treatment while the Zn2-Mg0.5 could still successfully pass the test after annealing. Microstructural analysis was then carried out on the annealed samples to study the reasons of the adhesion loss of the Zn2-Mg0.75 structure.

Fig. 1a shows the TEM micrograph of the Mg-Zn bi-layered coating (Zn2-Mg0.5) after annealing at 180 °C for 144 h. MgZn₂ intermetallic compound is formed due to the reaction of the pure Mg and the pure Zn. Pure Zn has a lower melting point (419 °C) than pure Mg (650 °C) and consequently Zn might require less activation energy to diffuse in Mg. The atomic radius of zinc (134 pm) is also smaller than that of Mg atoms (160 pm) which allows a faster diffusion of Zn atoms in Mg rather than Mg atoms in Zn [10]. Moreover, the solubility of Mg in Zn is extremely low according to the binary phase diagram [11]. Therefore, it seems that the upward diffusion of Zn from the zinc interlayer towards the top Mg layer is faster than the diffusion of Mg into the opposite side. This leads to the reduction of the thickness of the initial zinc interlayer during the annealing treatment. Similar behavior of higher diffusivity of Zn in Mg single crystals is also previously reported [10]. The thickness of the

remaining zinc interlayer after annealing the Zn2-Mg0.5 sample is about 1.1 μm . EDS analysis was performed to investigate the possible diffusion of Mg through the zinc interlayer. No sign of Mg was detected in the zinc interlayer after 144 h of annealing within the detection limit of EDS in the TEM. However, magnesium diffusion towards the steel substrate interface has been reported earlier [9]. Therefore, theoretical modelling of diffusion in Zn-Mg system is required in the future to address this phenomenon. At the same time, Fe diffuses from the steel substrate toward the top layer. The concentration of Fe in the zinc interlayer decreases with increasing the distance from the steel/Zn interface and reaches 6.3 wt.% close to the interface of ZnMg and Zn. It should be noted that 0.45 wt.% Fe was detected in the middle of the ZnMg layer that was formed by annealing (illustrated in Fig. 1a). It was also found that Fe-Zn intermetallic was formed as a continuous layer with the average thickness of 85 nm at the steel/Zn interface by the annealing treatment (Fig. 1b). No sign of any Fe-Zn intermetallics was found at the steel/Zn interface in the as-deposited Zn2-Mg0.5 coating (Fig. 1c). The formation of Fe-Zn intermetallic was reported to be detrimental for the adhesion of hot-dip galvanized coatings on steel substrate [12]. Meanwhile, since Zn2-Mg0.5 coating after the annealing treatment could pass the BMW crash adhesion test, it was concluded that the formation of Fe-Zn intermetallic phase does not play a significant negative role in the adhesion of the coatings in our investigation.

The cross section SEM micrograph of Zn2-Mg0.75 after 144 h of annealing is shown in Fig. 2a. The coating contains three different layers; zinc, $\text{Mg}_2\text{Zn}_{11}$ and MgZn_2 . Elemental line scan (Fig. 2b) supports the presence of two ZnMg layers with different Mg concentrations on top of the zinc interlayer. The thickness of the remaining zinc interlayer of Zn2-Mg0.75 after the annealing is in the range of 400 nm - 850 nm. It should be noted again that this sample failed in the BMW crash adhesion test. For both coatings, although some small voids were already observed in the as-deposited condition, but their density was low to cause a failure in

the BMW adhesion test. However after the annealing treatment and subsequent reduction of the thickness of the Zn interlayer, adhesion failure was observed in the annealed Zn2-Mg0.75 coating but not in the annealed Zn2-Mg0.5 coating. This emphasizes the role of the thickness of the remaining Zn interlayer on the adhesion performance.

Fig. 3a shows an example of Zn2-Mg0.75 failed in BMW crash adhesion test. The SEM micrograph of the exposed side of the coating attached to the glue (Fig. 3b) shows smooth regions as in Spot 1, bumpy regions as in Spot 2 and some small voids indicated by arrows. Table 3 summarizes the EDS results of different regions in Fig. 3. The dominant element in Spot 1 is Zn with a small amount of Fe. Meanwhile, Spot 2 contains both Fe and Zn. The SEM micrographs of the remained part of the coating on the steel substrate are presented in Fig. 3c and d. Spot 3 contains 88.1 wt.% Fe and 11.9 wt.% Zn, while Spot 4 is composed of Fe (as the substrate). The EDS elemental mappings of Fig. 3d are presented in Fig. 3e and f. No sign of Mg is detected on both the delaminated coating side and the exposed steel side, indicating that the delamination has definitely occurred across the zinc interlayer. Therefore, it seems that the diffusion of Mg does not play a significant role in the loss of adhesion for Zn2-Mg0.75 during the heat treatment. Instead, the reduction of the thickness of the zinc interlayer (t_{Zn}) by annealing seems to have a dominant role on the adhesion loss of ZnMg-Zn bi-layered coatings.

In order to further study the effect of t_{Zn} on the adhesion, ZnMg-Zn bi-layered coatings with three different thicknesses (0.2, 0.7 and 1.3 μm) of zinc interlayer were studied. Fig. 4 shows the cross-sectional SEM micrographs of the investigated ZnMg-Zn bi-layered coatings. The thickness and chemical composition of ZnMg top layer were kept constant for all the coatings to about 3 μm and 6.5 wt.% Mg, respectively. The XRD results revealed that the coatings contain a mixture of $\text{Mg}_2\text{Zn}_{11}$ phase as the main phase ($\sim 81\%$) and MgZn_2 as the second phase ($\sim 19\%$).

Scratch tests were performed to determine the adhesion strength of ZnMg-Zn bi-layered coatings at the ZnMg/Zn interface. Fig. 5a shows a typical acoustic emission curve versus the normal load applied in scratching the ZnMg-Zn bi-layered coating containing 0.7 μm thick zinc interlayer (Zn_{0.7}-ZnMg₃). Through-thickness cracks were found along the scratch groove before the delamination initiation of the ZnMg top layer (Fig. 5b). The ZnMg coating starts to delaminate from the interface of ZnMg/Zn at the critical load of 13.1 N, possibly due to the buckling phenomena, where the zinc interlayer is clearly visible ahead of each buckled region (Fig. 5c and d). The zinc interlayer is also delaminated from the steel substrate close to the end of the groove at 19.5 N normal load (Fig. 5e). The chemical compositions of the different phases in Fig. 5e are shown in Table 4.

Fig. 6a shows the critical load of delamination for the investigated ZnMg-Zn bi-layered coatings versus t_{Zn} . The critical load increases with increasing t_{Zn} from 11.6 N to 13.25 N. It was shown in our previous work [13] that the critical load (L_c) is not a suitable criterion to investigate the adhesion strength of the ZnMg-Zn bi-layered coatings containing different chemical composition and/or layers thickness ratios. Therefore, the modified Benjamin-Weaver model [13] was used to quantify the adhesion strength of the ZnMg-Zn coatings at the ZnMg/Zn interface:

$$F = \frac{KaH}{\sqrt{R^2 - a^2}} \quad (1)$$

where F is the adhesion strength at the ZnMg/Zn interface (MPa), K is a constant equal to 0.2, H can be considered as the hardness of the substrate, R is the radius of the indenter tip and a is the radius of the contact circle determined as

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

For the bi-layered coatings, the effect of both zinc interlayer and steel substrate should be considered in the parameter H mentioned above according to the proposed weight factor and composite hardness as follows:

$$\omega = \frac{t_{Zn}}{\text{Residual depth at } L_C} \quad (3)$$

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

The significance of the modified Benjamin-Weaver model used to quantify the interfacial adhesion strength is that by taking into account the composite hardness of the zinc interlayer and steel substrate in the model, the adhesion strength at the ZnMg/Zn interface can be estimated, which is the weakest in comparison with the adhesion of zinc interlayer to steels substrate. It is found that the adhesion strength at the ZnMg/Zn interface calculated by the developed model is around 110 MPa for the ZnMg-Zn bi-layered coatings containing 6.5 wt.% Mg in the top layer and is independent of the t_{Zn} (see Fig. 6b). Although the adhesion strength of all three investigated ZnMg-Zn coatings was nearly the same, the coating with the smallest t_{Zn} failed in the BMW crash adhesion test while others successfully passed the test. In the failed sample, t_{Zn} was less than 10 % of the total thickness of the coating. It seems that such a thin zinc interlayer cannot accommodate the deformation, leading to the failure of the coating in the BMW crash adhesion test.

Zn0.7-ZnMg3 was then annealed at 180 °C for different durations to intentionally reduce t_{Zn} in order to scrutinize the role of the thickness of the interlayer on the adhesion. It is worth to mention that the SEM observations show no detectable change of the grain size of ZnMg top layer before and after the annealing. Fig. 7 shows the cross sectional SEM micrographs of Zn0.7-ZnMg3 annealed for 15 h, 48 h and 96 h, respectively. Increasing the annealing time results in the reduction of t_{Zn} . Moreover, the reduction of the thickness is not homogenous but with a fluctuant interface. The Mg concentration and thickness of ZnMg layer as well as the thickness of zinc interlayer are summarized in Table 5. The thickness of the zinc interlayer after 15 h annealing is ranged in 200 - 450 nm with an average value of 350 nm. At the same

time, it is found out that the thickness of the ZnMg top layer is increased to 3.3 μm , while its Mg concentration is decreased to 6.1 wt.% from the initial Mg concentration of 6.5 wt.% in the as-deposited coating. Increasing the annealing time to 48 h leads to further reduction of the thickness of Zn interlayer to an average value of 250 nm, which can reach to less than 100 nm in some regions. The Mg concentration of the top layer is also decreased to 5.9 wt.%. Zinc interlayer disappears in some parts of the interface after 96 h annealing. The overall thickness of the bi-layered coatings (Zn interlayer + ZnMg top layer) is almost constant after annealing for different times. These results indicate that the diffusion of zinc toward the top layer is dominant compared to possible diffusion of Mg from the top layer toward the substrate. Although the adhesion strength of ZnMg_{6.5}/Zn bi-layered coating annealed for 15 h is 115 MPa, slightly higher than 111 MPa of the as-deposited coating sample, all of the annealed samples failed in the BMW crash adhesion test. Fig. 8 shows the SEM micrographs of the delaminated surface of 15 h annealed Zn_{0.7}-ZnMg₃ bi-layered coating attached to the substrate after BMW crash adhesion test. As seen, delamination is partially occurred at the interface of Zn/steel and also at the interface of ZnMg/Zn, possibly depending on the thickness of the remaining Zn interlayer after annealing. Considering that all of the annealed samples failed in the BMW crash adhesion test, the obtained results indicate that t_{Zn} plays the predominant role in the adhesion of ZnMg-Zn bi-layered coating during the annealing treatment.

4. Conclusions

In the present study a novel view was attained on the adhesion loss of ZnMg-Zn bi-layered coatings during the annealing process. The new findings of the present investigation are summarized as follows:

- The thickness of the zinc interlayer (t_{Zn}) plays the dominant role in the adhesion performance of ZnMg-Zn bi-layered coating systems, while the adhesion strength at the ZnMg/Zn interface of the as-deposited system is independent of the thickness of the zinc interlayer.
- The thickness of the zinc interlayer decreases gradually during annealing at 180 °C as the consequence of zinc dissolution and diffusion.
- The adhesion performance of the coating system drops drastically when the thickness of the zinc interlayer is less than ~ 500 nm, as tested by BMW crash adhesion test.
- Although the diffusion of the elements across the coating during annealing at 180 °C can slightly increase the adhesion strength at the ZnMg/Zn interface, the concurrent reduction of the thickness of the zinc interlayer can significantly deteriorate the adhesion performance of the coating.

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Table 1 Chemical compositions (wt.%) of the steel substrates

	C	Si	Mn	P	S	Ni	Cr	Cu	Fe
DP800	0.153	0.386	1.487	0.013	0.007	0.018	0.022	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.

Table 2 Summary of the Mg-Zn and ZnMg-Zn bi-layered coatings as-produced in this research

	Thickness of zinc interlayer (μm)	Thickness of Mg top layer (μm)	Thickness of ZnMg top layer (μm)	Results of BMW adhesion test
Zn2-Mg0.5	2	0.5	-	pass
Zn2-Mg0.75	2	0.75	-	pass
Zn0.2-ZnMg3	0.2	-	3	fail
Zn0.7-ZnMg3	0.7	-	3	pass
Zn1.3-ZnMg3.1	1.3	-	3.1	pass

Table 3 Chemical composition of different points in Fig. 3b and c.

Location	Zn content (wt.%)	Fe content (wt.%)	Mg content (wt.%)
Spot 1	90.1	9.9	0
Spot 2	35.5	64.5	0
Spot 3	11.9	88.1	0
Spot 4	0	100	0

Table 4 Chemical composition of different phases shown in Fig. 5e

Location	Zn content (wt.%)	Fe content (wt.%)	Mg content (wt.%)
Zn	100	0	0
Fe	0	100	0
ZnMg	92.85	0	7.15

Table 5 Characteristics of the ZnMg_{6.5}-Zn bi-layered coating and the result of the BMW crash adhesion test by annealing at 180 °C for different durations.

Annealing duration (h)	Thickness of the zinc interlayer (μm)	Thickness of the ZnMg top layer (μm)	Mg concentration in ZnMg top layer (%)	Result of BMW crash adhesion test
0	0.7	3	6.5	pass
15	0.35	3.3	6.1	fail
48	0.25	3.4	5.9	fail
96	0.15	3.5	5.7	fail

Fig. 1 TEM micrographs of Zn₂-Mg_{0.5} bi-layered coating: (a, b) annealed at 180 °C for 144 h, (c) as-deposited.

Fig. 2 Cross sectional SEM micrograph of Zn2-Mg0.75 bi-layered coating annealed at 180 °C for 144 h along with the elemental line scan.

Fig. 3 (a) an example of Zn₂-Mg_{0.75} failed in BMW crash adhesion test along with the SEM micrograph showing the delaminated coating attached to the glue (b), (c and d) partial Zn interlayer remained on steel substrate, (e and f) EDS elemental mapping of (d).

Fig. 4 SEM micrographs showing the cross section of ZnMg-Zn bi-layered coatings with various t_{Zn} : (a) Zn_{0.2}-ZnMg₃, (b) Zn_{0.7}-ZnMg₃ and (c) Zn_{1.3}-ZnMg_{3.1}.

Fig. 5 (a) acoustic emission curve versus normal load obtained for Zn_{0.7}-ZnMg₃ bi-layered coating during the scratch test, SEM micrographs at different normal loads: (b) Point 1, (c, d) Point 2 and (e) Point 3.

Fig. 6 (a) critical load and (b) adhesion strength of ZnMg-Zn bi-layered coatings containing 6.5 wt.% Mg in the top layer versus thickness of the zinc interlayer.

Fig. 7 Cross section SEM micrographs of the Zn_{0.7}-ZnMg₃ bi-layered coating after annealing at 180 °C for different duration: (a, b) 15 h, (c, d) 48 h, and (e, f) 96 h.

Fig. 8 SEM micrographs showing some spots of remaining Zn interlayer attached to the steel substrate after BMW crash adhesion test on the 15 h annealed Zn_{0.7}-ZnMg₃ bi-layered coating.

Highlights:

- ZnMg-Zn bi-layered coatings with different Zn interlayer thicknesses deposited by thermal vapor deposition
- The adhesion of the ZnMg-Zn bi-layered coatings is investigated by scratch and BMW crash tests
- A modified model proposed to quantify the adhesion strength of ZnMg-Zn bi-layered coatings
- The thickness of zinc interlayer plays a predominant role on the adhesion performance of ZnMg-Zn bi-layered coatings