Zn–Mg coatings with Mg compositions ranging from 5 wt.% to 15 wt.% were synthesized on high-strength steels using the electromagnetic heating deposition process, and the effects of a 1-μm thick Zn interlayer on the formability and adhesion of the Zn–Mg coatings were investigated. The Zn–Mg coatings with the Zn interlayer showed little difference in terms of microstructure, crystal structure and corrosion resistance compared to the Zn–Mg coatings without the Zn interlayer. In contrast, the Zn interlayer significantly contributed to the improvement of the formability and adhesion of the Zn–Mg coating. The delamination area of the Zn–Mg coating with the Zn interlayer after deformation was extensively reduced, and the results of the lap shear tests revealed that the maximum adhesion strength of the Zn–Mg coatings with the Zn interlayer was approximately twice as high as that of the Zn–Mg coatings without the Zn interlayer. The maximum adhesion strength of the Zn/Zn–Mg coatings with 15 wt.% Mg, which showed the best corrosion resistance was measured to be slightly over 10 MPa, pending more research to increase the adhesion strength of the Zn–Mg coatings with high content of Mg over approximately 20 MPa necessary.

KEY WORDS: Zn–Mg coatings; microstructure; corrosion resistance; adhesion strength; formability; TRIP steel.
strength of the coating should be considered equally important as the Zn–Mg coated steels are inevitably subjected to the extensive forming process such as punching, bending, press forming etc. Recently several papers were reported on the adhesion strength of Zn–Mg coatings on steel. Lee et al. reported the Al interlayer could provide with improved adhesion between the Zn–Mg coating and Al interlayer via precise metal bonding.\(^{15}\) Systematic investigation on the effect of the Mg content (0 to 15 wt.\%) on the adhesion strength of Zn–Mg alloy coatings on steel was provided by Jung et al. using a lap shear test.\(^{16}\) In their report, the adhesion strength of Zn–Mg alloy coatings on the steel strip is strongly dependent upon the total content of Mg in the coating, varying from 16.34 MPa for 3\% Mg coating (similar to GI 60 g/m\(^2\)) to 7.77 MPa for coatings with more than 9 wt.\% Mg. Zoestbergen et al. produced a double layer Zn–Mg coatings with a bottom Zn film and a top Mg film and annealed the coating at 175°C to investigate the influence of Zn and Mg diffusion on the adhesion behavior of Zn–Mg coatings on steel using the crash adhesion tests. They showed that the segregation of magnesium to the steel-zinc interface during the annealing plays an important role in the crash adhesion performance of the coatings, suggesting the Zn film is necessary to improve the time to failure.\(^{17}\) Byun et al. produced Zn–Mg–Zn multi-layer coating by depositing Zn, Mg and Zn layers sequentially on the surface of a steel sheet using PVD process and investigated the effect of the annealing heat treatment at 200°C on the adhesion behavior of the coating via OT-bending test.\(^{18}\) They showed that as annealing time increased the volume fraction of the brittle intermetallic compounds such as Mg\(_2\)Zn\(_{11}\) and MgZn\(_2\) phases increased, resulting in the poor adhesion behavior of the coatings. Recently, La et al. reported that the adhesion strength of Zn–Mg coating with high Mg content could be improved by increasing the substrate temperature during the magnetron sputtering process. In their paper, the increased substrate temperature provided with an annealing effect on the amorphous microstructure of Zn–Mg coating with high Mg content to become a crystalline structure consisting of a MgZn\(_2\) intermetallic phase and (Zn) solid solution phase.\(^{19}\)

As mentioned above, the previous reports mainly focused on the Mg composition or annealing effect on the adhesion strength of the Zn–Mg coating. Even though the insertion of an interlayer would be one of the most effective methods to improve the adhesion strength of coating, the effect of Zn interlayer between the substrate steel and the Zn–Mg coating was not reported yet. Therefore in this study, a Zn interlayer with a 1-μm thickness was synthesized between Zn–Mg coatings and high-strength steel using the PVD process and the adhesion behaviors of the Zn–Mg coatings with the Zn interlayer (Zn/Zn–Mg coatings) were investigated quantitatively. In addition the effect of the Zn interlayer on the corrosion resistance of the Zn–Mg coating was examined via a potentiodynamic polarization test.

### 2. Experimental Details

Zn–Mg coatings and Zn/Zn–Mg coatings were deposited on Si wafers and high-strength steel (HSS) using the energy-efficient electro-magnetic heating deposition (EMHD) process.\(^{19}\) To synthesize the Zn–Mg coatings and Zn/Zn–Mg coatings with various chemical compositions, spherical Zn and Mg bullets (16 mm Ø, 99.9% purity) with various ratios were evaporated using an induction heating system with a high frequency power of 3.0 kW at 81 Hz. For the HSS substrates, commercial TRIP steel (1180CP, POSCO, chemical composition (wt.\%) = C\(<\)0.17\%, Mn\(<\)2.8\%, Si\(<\)0.25\%, P\(<\)0.02\%, S\(<\)0.005\%, Fe remainder, thickness = 1.2 mm) was used after cleaning ultrasonically in an alcohol solution for 30 minutes. Before deposition Ar plasma etching was done to remove the surface oxide. The temperature of the chamber and the internal pressure was maintained at 200°C and 5.0×10\(^{−5}\) Pa, respectively.

The microstructures and the crystal structure of the coatings were analyzed using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7100F) with an energy dispersive X-ray spectroscopy (EDS) and an X-ray diffractometer (XRD, Rigaku MiniFlex II) with Cu Kα irradiation (λ = 0.15456 nm).

A potentiodynamic polarization test at room temperature in a stagnant 3.5\% NaCl solution was conducted using a commercial potentiostat (PAR VersaSTAT III) at a scan rate of 5 mV/s from an initial cathodic potential of −2.00 V\(_{SCE}\). A conventional three-electrode cell was used. A Pt mesh and a saturated calomel electrode (SCE) were used as a counter electrode, and as a reference electrode, respectively and the coated steel with 1 cm\(^2\) surface area was used as a working electrode. A tafel plot (log i vs. E plot) was used to measure the corrosion potential (E\(_{corr}\)) and corrosion current density (i\(_{corr}\)).

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**Table 1.** Schematic diagrams of punch stretching test and lap shear test. (Online version in color.)

| Punch test | Lap shear test |
| --- | --- |
| ![Punch test](image) | ![Lap shear test](image) |

- Deformation depth : 10 mm
- Strain : 0.35
- Adhesive : structural epoxy-type adhesive
- Shear strength of adhesive : 21 MPa

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A punch stretching test (ASTM E643-15) and lap shear test (ASTM D1002) were carried out to investigate the formability and adhesion of the Zn–Mg and Zn/Zn–Mg coatings, respectively. The schematic diagrams of the punch stretching test and lap shear test are shown in Fig. 1. The dimensions of the specimens for the punch stretching test were 50 mm × 30 mm × 1.2 mm, and the punched depth was 10 mm, which was approximately 35% strain. After the test, the delamination area at the center of the deformed area was calculated using an optical microscope (OM, Olympus BX 51M). The lap shear test was carried out to determine the quantitative shear strength of the coated sheet. The dimensions of specimens for the lap shear test were 100 mm × 25 mm × 1.2 mm. The structural epoxy-type adhesive (25-MPa shear strength, BOKWANG Co., N.F.W Hemming Sealer) was used to bond the two Zn–Mg coated steels with a 25 mm × 25 mm overlap area, as shown in Fig. 1. The single lap joints were tested in a tensile testing machine (Shimadzu, AG-10TA) using a displacement rate of 5 mm/min.

3. Results and Discussion

The Zn–Mg coatings with various Mg compositions were synthesized using the EMHD process with a high deposition rate of 1 μm/min, which was approximately 15 times higher than that of the conventional sputtering process. The total thickness of the coatings was 3 μm and the Zn interlayer was 1 μm thick for Zn/Zn–Mg coatings. The cross-sectional microstructures of the various Zn–Mg and Zn/Zn–Mg coatings were examined as shown in Fig. 2. In the case of the Zn-5 wt.% Mg coating, the porous microstructure was synthesized, while the Zn-10 wt.% Mg coating showed a columnar structure. The Zn–Mg coating with a high Mg content of 15 wt.% showed a featureless structure. This featureless microstructure was determined to be an amorphous structure and will be explained in detail in the next paragraph. Figures 2(d)–2(e) show the cross-sectional microstructures of the Zn/Zn–Mg coatings. Despite the presence of the Zn interlayer, the microstructure transition tendency of the Zn–Mg coatings on the Zn interlayer as a function of the Mg composition was similar to that of the Zn–Mg coating without the Zn interlayer.

The X-ray diffraction (XRD) patterns from the Zn–Mg coatings are shown in Fig. 3. In the case of the Zn-5 wt.% Mg coating, the peaks from the Zn phase were observed clearly, while other phases were not detected due to the small Mg content, suggesting (Zn) solid solution. In the Zn-10 wt.% Mg coating, peaks from intermetallic phases such as Mg2Zn11 and MgZn2 were observed. However, the XRD pattern from the Zn-15 wt.% Mg coatings indicated that the crystal structure of the coating changed from crystalline to amorphous. The formation of the amorphous phase in the Zn–Mg coatings with high Mg contents has previously been reported. In the Mg–Zn binary system, various intermetallic phases such as Mg2Zn11 and MgZn2 served as equilibrium phases in a Mg content range from 0 wt.% to 15 wt.%. However, the solid solubility of Mg in (Zn) was extended by very high cooling rate (about 10¹² K/s) during the PVD process. Dai et al. also reported that when the Mg content exceeded 15 wt.%, the crystal structure of (Zn) was able to transform into an amorphous state due to the difference in the atomic size between Mg and Zn atoms. The formation of the amorphous phase in the Zn-15 wt.% Mg coatings was also consistent with that Zn-15 wt.% Mg (Zn-32.3 at.% Mg) composition was well within the glass forming composition range of 21–87 at.% Zn in Zn–Mg binary system, which was calculated using Egami and Midema et al. approaches. In all of the Zn–Mg coatings with the Zn interlayer, as shown in Fig. 3(b), the intensity of the Zn peak appeared, which was due to the influence of the crystalline Zn interlayer. In the case of the Zn/Zn-10 wt.% Mg coating, there existed the same Zn–Mg alloy intermetallic peaks with Zn-10 wt.% Mg coating such as Mg2Zn11 (210), (222), (321), (410), (411) and MgZn2 (112), (104). In the Zn/Zn-15 wt.% Mg coating, only the peaks from the Zn interlayer were observed due to the amorphous structure of the Zn-15 wt% Mg coating. The insertion
of Zn interlayer did not induce significant change in terms of microstructure and crystal structure, except a presence of Zn peak due to Zn interlayer.

To investigate the corrosion resistance of the Zn–Mg coatings and the Zn/Zn–Mg coatings, the potentio-dynamic polarization test was carried out. Figure 4 shows the polarization curves of the coatings, and the corrosion parameters are summarized in Table 1. The corrosion current density of the Zn-5 wt.% Mg coating was 6.96 μA/cm², and the corrosion current density decreased to 1.91 μA/cm² as the Mg content of the coating increased to 15 wt.%. The corrosion potential of the Zn-5 wt.% Mg coating was −1.33 V SCE, which also increased to −0.76 V SCE with the increasing Mg content. Zn–Mg coating with increasing Mg content became more noble and the corrosion rate became reduced. These results confirmed the previously reported results, in that as the Mg content of coatings increased, the corrosion resistance of the Zn–Mg coatings increased, which could be attributed to the transition of the microstructure of coatings from porous to dense and featureless, amorphous structure.10,24) The increment of corrosion resistance as a function of Mg content in the Zn–Mg coatings could be explained with the dense microstructure and intermetallic phase, as shown in Figs. 2 and 3. Single intermetallic phases, Mg2Zn11 and MgZn2 were reported to improve the corrosion properties compared to pure Zn solid solution phase25) and these phase in the Zn-10 wt.% Mg coatings contributed the improved corrosion resistance compared to Zn-5 wt.% Mg coating. As the microstructure of the coating was a parameter that determined the corrosion protection ability of the coating to a greater extent than the intermetallic compounds in the Zn–Mg coatings,26,27) the Zn–Mg coatings with 15 wt.% Mg which had an amorphous microstructure showed the best corrosion resistance. Figure 4(b) shows that the Zn/Zn–Mg coatings exhibited similar corrosion resistance to the Zn–Mg coatings because they possessed the same micro-

| Mg composition (wt.%) | Zn–Mg coating | Zn/Zn–Mg coating |
|-----------------------|---------------|------------------|
|                       | Vcorr (V SCE) | Icorr (μA/cm²)  | Vcorr (V SCE) | Icorr (μA/cm²) |
| 5                     | −1.33         | 6.96             | −1.39         | 5.89           |
| 10                    | −1.25         | 1.91             | −1.19         | 1.26           |
| 15                    | −0.76         | 1.49             | −0.59         | 1.19           |

Fig. 3. The X-ray diffraction patterns of the Zn–Mg and Zn/Zn–Mg coatings synthesized with various Mg contents: (a) Zn–Mg XRD pattern, (b) Zn/Zn–Mg XRD pattern. (Online version in color.)

Fig. 4. The potentio-dynamic polarization curves of the Zn–Mg and Zn/Zn–Mg coated steels measured in a 3.5% NaCl solution: (a) Zn–Mg coatings, (b) Zn/Zn–Mg coatings.
The corrosion current densities of the Zn/Zn–Mg coatings changed from 5.89 μA/cm² to 1.55 μA/cm², and the corrosion potential increased from −1.39 to −0.59 V SCE when the Mg content increased from 5 wt.% to 15 wt.%. The insertion of a Zn interlayer between the substrate and the Zn–Mg coatings did not show a detrimental effect on the corrosion resistance of the Zn–Mg coatings, but in fact a slightly improved corrosion resistance was resulted as shown in Table 1 and this could be attributed to the additional interphase boundary effect in the Zn/Zn–Mg coatings.

The punch stretching test and lab shear test were performed to evaluate the formability and adhesion of the Zn–Mg and Zn/Zn–Mg coatings, and the results are shown in Figs. 5 and 6, respectively. Figure 5 shows the OM observations at the center of the deformed area after the punch stretching test. In the case of the Zn-5 wt.% Mg coating, cracks occurred in most areas of the coating surface after deformation, but delamination was not observed. As the Mg content of the coating increased to 10 wt.%, the delamination of the coating was observed, as shown in Fig. 5(b), and the delamination area was calculated to be 24.3% of the coating surface. The Zn-15 wt.% Mg coating showed the highest delamination area at 79.2% of the coating surface after deformation. The decrement of formability could be attributed to the crystal structure of the Zn–Mg coating transformed as a function of the Mg composition. The metallic coating with an amorphous structure like the Zn-15 wt.% Mg coatings showed brittle properties, which led to delamination during the deformation.20,28) Figures 5(d)–5(f) show the OM observations at the deformation center of the Zn/Zn–Mg coatings. When the Zn interlayer was deposited, however the delamination area was not observed in all cases. The Zn interlayer improved the bonding behaviors between the Zn–Mg coating and the substrate during deformation and inhibited the delamination.

The lab shear test was performed to quantitatively investigate the adhesion strength of the coatings. Figure 6 shows the tensile graph of the Zn–Mg coatings and the Zn/Zn–Mg coatings (also see Supplementary data). The maximum adhesion strength was 13.02 MPa in the Zn-5 wt.% Mg coating, and this value gradually decreased to 3.80 MPa as the Mg content increased to 15 wt.%. The fracture displacement decreased from 0.68 mm to 0.22 mm as the Mg content in the Zn–Mg coating increased. This decrease in the maximum adhesion strength and fracture displacement depending on the Mg composition indicated the decrement of adhesion and formability, which was similarly shown in the punch stretching test. The decreasing adhesion strength could be explained by the crystal structure transition of the coatings. The Zn-5 wt.% Mg coating showed a similar crystalline structure to that of the pure Zn, which changed
to a crystalline structure consisting of intermetallic phases such as Mg$_2$Zn$_{11}$ and MgZn$_2$ in the Zn-10 wt.% Mg coating.

Previous work reported that the adhesion strength of the Zn–Mg coating with 7 to 13 wt.% decreased compared to the Zn-3 wt.% Mg coating due to the intermetallic phases. As the intermetallic phases were formed in the Zn–Mg coating with high Mg content above 7 wt.%, the brittleness of the coating increased, which led to the decrement of the adhesion property. The Zn-15 wt.% Mg coating had an amorphous structure, as shown in Fig. 3, and this structure had high brittleness and low elongation compared to the crystalline structure. Therefore, when the lap shear test was performed, the adhesion strength of the amorphous coating was lower than that of the crystalline coating. In the case of the Zn/Zn–Mg coatings, the maximum adhesion strengths were in the range of 10.85 MPa to 23.94 MPa, and the fracture displacements were in the range 0.54 mm to 1.38 mm. When the Mg content of the Zn–Mg coating increased, the maximum adhesion strength and fracture displacement decreased. However, the maximum adhesion strengths and fracture displacements of the Zn/Zn–Mg coatings increased by 172–285% and 155–245%, respectively, compared to the Zn–Mg coating without the Zn interlayer. The Zn interlayer was able to suppress the delamination during deformation and drastically improve the adhesion characteristics, even if the Mg content of the Zn–Mg coating increased and the crystal structure of the coating changed to an amorphous structure. These results showed the extensive improvement of the adhesion and formability of the Zn–Mg coating via the Zn interlayer deposition could be possible.

4. Conclusion

Zn–Mg coatings in a Mg composition range from 5 wt.% to 15 wt.% were deposited via an EMHD process with a high deposition rate of 1 μm/min, and deposited was a 1-μm thick Zn interlayer between the substrate and the Zn–Mg coating to improve the formability and adhesion of the coating. When the Mg composition of the Zn–Mg coating increased from 5 wt.% to 15 wt.%, the microstructure of the coating changed from a porous structure to a featureless structure, and the crystal structure changed from a crystalline to an amorphous structure. The corrosion resistance of the Zn–Mg coatings increased with the increasing Mg content. The Zn/Zn–Mg coatings showed a similar chemical composition, crystal structure and corrosion resistance to the Zn–Mg coatings, even when the Zn interlayer was deposited. The adhesion evaluation results revealed that the adhesion and formability of the Zn–Mg coatings could be improved extensively via the deposition of the Zn interlayer, and the Zn/Zn–Mg coating exhibited a maximum adhesion strength that was approximately double that of the Zn–Mg coatings in the lap shear tests. However, the maximum adhesion strength of the Zn/Zn–Mg coatings with 15 wt.% Mg, which showed the best corrosion resistance was measured to be slightly over 10 MPa, which is far less than the required adhesion strength for automobile applications. According to the previously reported paper, the adhesion strength by lap shear test of conventional pure Zn electro-galvanized coating (EG) and hot-dip galvanized coating (GI) coatings on steel showed about 16 to 19 MPa. Therefore, more research is necessary to increase the adhesion strength of the Zn–Mg coatings with high content of Mg over approximately 20 MPa is still necessary to replace EG and GI coatings with Zn–Mg coatings by EMH PVD process on commercial industry.

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