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Simultaneous Co-deposition of Zn-Mg Alloy Layers on Steel Strip by PVD Process

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This is the first release of an interim report on the development of coating technology of Zn-Mg alloy layers on steel strip by EML-PVD (electromagnetic levitation - physical vapor deposition) process in an air-to-air type continuous PVD pilot plant. It intends to introduce a basic principle of the EML-PVD process together with the high speed PVD pilot plant built in Posco. Due to the agitation effect provided by the high frequency induction coil, simultaneous evaporation of Zn and Mg from a droplet could produce alloy coating layers with Mg content of 6% to 12% depending on the composition of the droplet inside the coil. For its superior corrosion resistance, Zn-Mg alloy coated steel would be a very promising material for automotive, electrical appliances, and construction applications.

Keywords *: Zn-Mg alloy deposition, EML-PVD, continuous strip coating*

1. Introduction

Zn-Mg alloys have been recognized as very effective layer for protecting steel product against corrosion.[1)] Several approaches has explored Zn-Mg coating by PVD processes, such as thermal evaporation and sputtering, which were restricted by physical limitations of vapor pressure difference and dynamic deposition rate for commercial application.

As an alternative to the PVD Zn-Mg coating, hot-dip Zn-Al-Mg coatings with less than 3 wt.% Mg in the layer were developed as well as Zn-Mg alloy layers produced from a combination of PVD Mg deposited onto an existing electrolytic Zn layer followed by post heating process.[2)] However, there has been a desire to produce a thin, higher Mg content layer, simultaneously from a single PVD source, which would reduce process complexity and cost.

The EML-PVD technology, which was introduced around ten years ago, can be an unique solution to satisfy the desire.[3)] As shown in Fig. 1, it is a kind of evaporation technology utilizing induction coil combined with a high frequency power supply, which provides induced current to levitate metal droplet inside the coil and to heat the droplet up. The vapor generated from the surface of the droplet is guided by a vapor distribution box, which evenly distributes the vapor to the steel strip moving above it. The metal evaporated can be supplemented by liquid metal fed from the bottom of the induction coil.

There is the third function of the induced current, the agitation, which can mix up zinc and magnesium uniformly in liquid state. This can yield simultaneous co-deposition of Zn-Mg alloy from a single source by keeping the surface composition the same all the time. It is also possible to maintain the vapor composition the same as that of liquid metal fed from outside of the vacuum chamber.

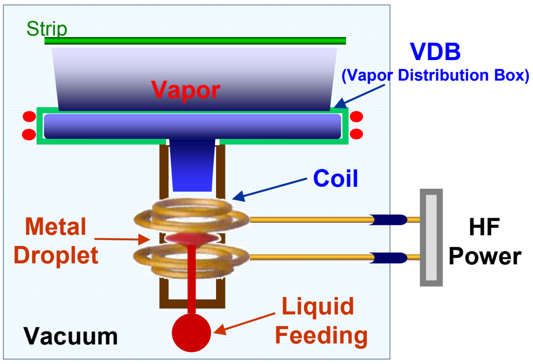

Fig. 1. Schematic drawing of the structure of EML-PVD evaporation source.

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This paper deals with the co-deposition behaviour of Zn-Mg coating layers by the EML-PVD technology, which were validated from operation of a high speed air-to-air PVD pilot plant, and confirms the superior corrosion resistance of the Zn-Mg coating layers.

2. Facility setup

2.1 PVD pilot plant

Air-to-air type PVD pilot and production plants, which allows continuous passing of a strip into and out of the vacuum chamber without breaking the vacuum have been reported in the literature[4),5)] and have found industrial application, particularly in the coating on Aluminum strip.[6)]

Photo. 1 shows the overall view of the pilot plant built in Posco. It starts from the entry side of strip handling, a pay-off reel and a welder, followed by an entry strip-lock chambers which can guide the strip into the vacuum chamber continuously. There are six lock chambers in the entry and seven in the exit side. After entering into the vacuum, the strip is cleaned and activated by plasma pretreatment, which utilize Argon (Ar) plasma from six inverse magnetron sputter etchers.

There are two separate coating chambers after the pretreatment, an EB-PVD chamber and an EML-PVD chamber. In EB chamber, there are two EB guns of 200 kW each, which have dual functions of evaporation and strip preheating. In EML chamber, an EML evaporation source of 300 kW with 1.6 kg of droplet is installed inside. Through the exit strip-lock chambers, the strip comes out from the vacuum, followed by exit side of strip handling, a shear and a tension reel. Main feature of the pilot plant is its maximum speed of 200 mpm with 300 mm wide strip and gauge of up to 2 mm. It will allow the development of a high productivity process which can compete with existing coating lines, such as CGL and EGL.

Photo. 1. Overall view of PVD pilot plant.

2.2 EML-PVD evaporation source

To make a Zn-Mg coating layer of three micron thick on 300 mm wide strip at running speed of 200 m/min, it is necessary to evaporate approximately 60 kg/hr of Zn-Mg alloy by the evaporation source. By an empirical equation, it needs 1.6 kg of Zn-Mg droplet to be levitated to provide sufficient surface area for the evaporation rate.

Photo. 2 shows the shape of a droplet levitated in open-air. It is a zinc droplet of 1.6 kg, which can prove enough levitation capability of Zn-Mg alloy in vacuum. Special design of the induction coil combined with a heavy-duty high frequency power supply can levitate the heavy droplet.

When enough vapor is generated from the droplet, it should be guided uniformly to the surface of the steel strip. The basic concept underlying the design of a vapor distribution box is to build choking condition of the vapor. Simply it can be understood in terms of the pressure difference between inside and outside of the VDB. If the difference is higher than 100 times, the choking condition can be build up and the vapor flow distribution along the VDB width would be uniform regardless of the configuration of the nozzle of VDB.

Photo. 3 shows a result of numeric simulation of vapor flow inside and outside of the VDB. The color indicates flow velocity of the vapor. Under choking condition, the

Photo. 2. Open-air levitation of a droplet.

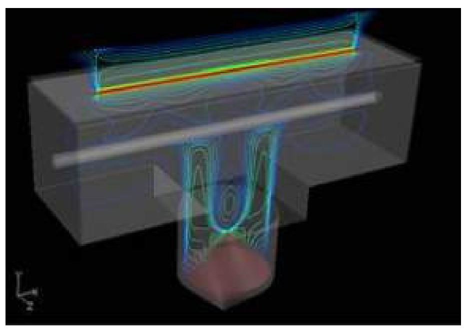

Photo. 3. Simulation of flow pattern from a VDB.

vapor flow out of the VDB is very uniform along the width of the VDB, and the vapor is directed to perpendicular direction without diffusing elsewhere. It can be demonstrated by the analysis of coating thickness and composition.

3. Experimental results

3.1 Simultaneous Co-deposition of Zn-Mg alloy layers

Photo. 4 shows the steel strip coated with Zn-Mg alloy of 8 ~ 9 wt.% Mg. The color of the coating layer was light gray with metallic glossiness. The profile of coating thickness and composition along the strip width were very uniform, less than 5% deviation, as shown in Fig. 2. The coating thickness was expressed by dynamic deposition rate, the thickness multiplied by strip speed.

It is possible to demonstrate the simultaneous co-deposition of Zn-Mg alloy layer from a single source by cross-sectional morphology (Photo. 5) and GDS depth profile (Fig. 3) of a Zn-Mg coating layer with 14 wt.% Mg content. In Photo 5, there is no intermission in the layer, which indicates that it was formed by a single stage condensation process. In GDS analysis, the composition of the layer was very uniform through the whole layer thickness.

Considering very high vapor pressure of zinc, which is nearly 10 times higher than that of magnesium, it would be impossible to make an alloy coating layer. It is not fully understood yet, but a kind of gathering effect of zinc evaporation seems to promote the evaporation of magnesium to allow enough magnesium to be co-deposited with zinc. When it is possible to keep the surface concentration of a droplet constant, it can produce constant coating composition for continuous operation.

3.2 Structure of the Zn-Mg alloy coating layers

Photo 6 shows the surface morphology of Zn-Mg coat-

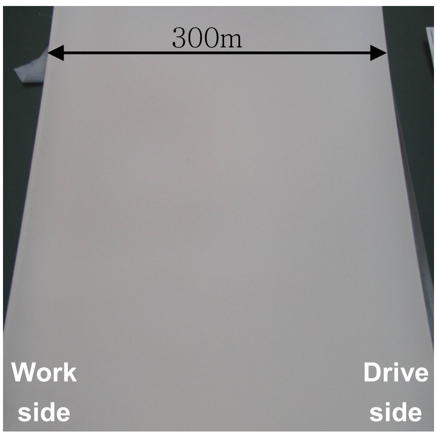

Photo. 4. Steel strip coated with Zn-Mg alloy layer.

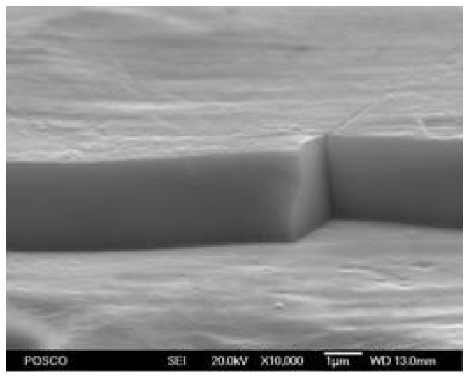

Photo. 5. Cross-sectional morphology of Zn-Mg alloy coating layer (x10,000).

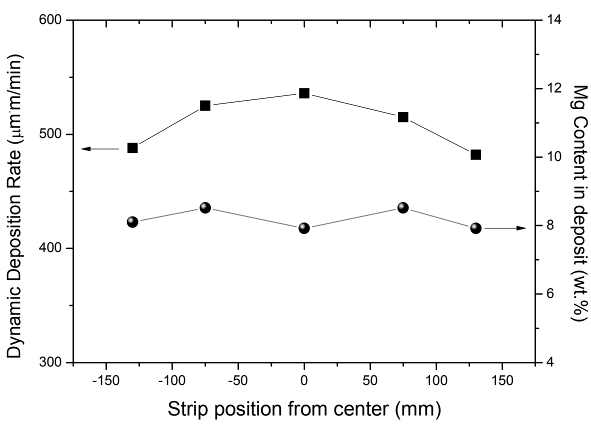

Fig. 2. Profiles of coating thickness and composition along the strip width.

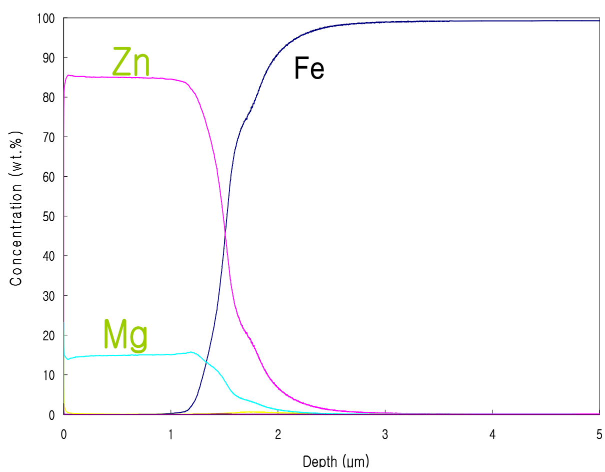

Fig. 3. GDS depth profiles of Zn-Mg alloy coating layer.

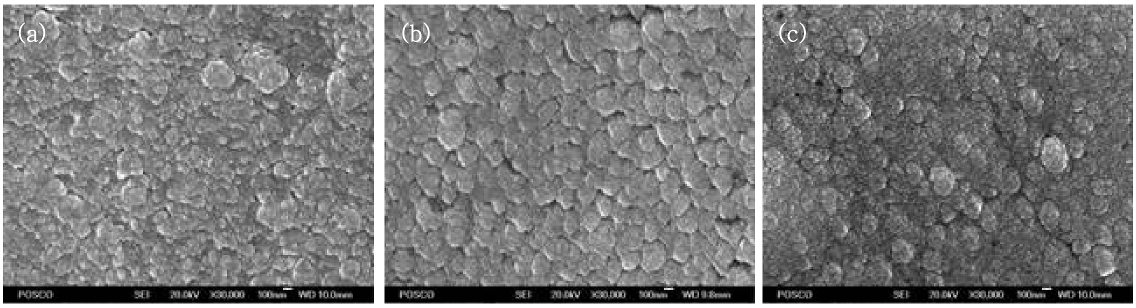

Photo. 6, Morphology of Zn-Mg coating layers (x 30,000) (a) 5.1 wt.% Mg, (b) 9.3 wt.% Mg, (c) 14.1 wt.% Mg.

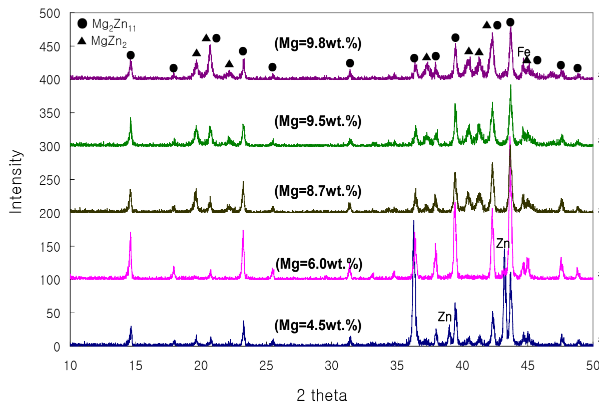

Fig. 4. X-ray diffraction patterns of Zn-Mg alloy coating layers.

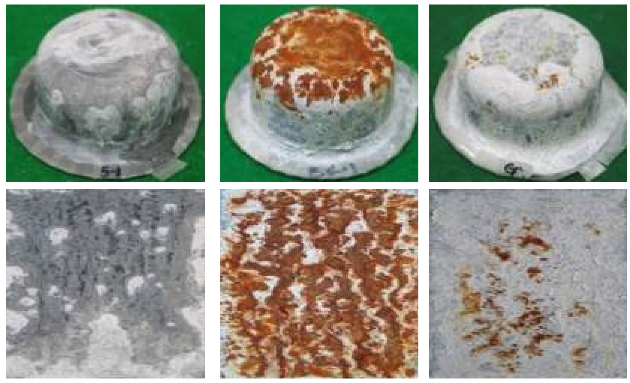

Photo. 7. Corrosion resistance of drawn (upper) and flat (bottom) specimens after 240 hours salt spray test
(a) Zn-Mg (9.2 wt.% Mg) 20 g/m^2, (b) EG 60 g/m^2, (c) GI 60 g/m^2.

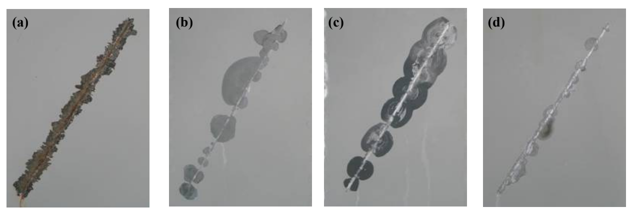

Photo. 8. Blister formation of electopainted and scribed specimens after salt spray test for 480 hours
(a) GA 45g/m^2, (b) EG 60g/m^2, (c) GI 60 g/m^2, (d) Zn-Mg (9.2wt.% Mg) 20 g/m^2.

ing layers with variation of the coating composition. There are no significant changes in the morphology with composition, but the size of grains are very fine, only a few hundred nanometer in average.

The phases of the Zn-Mg coating layers with different coating composition are shown in Fig. 4. The main phases of the Zn-Mg alloy are Mg_2Zn_{11} and $MgZn_2$ intermetallic compounds. In the range of 6 ~ 10 wt.% Mg, there is a little difference in the relative intensity of the phases, which indicate the increase of $MgZn_2$ peak intensities. When the composition was lower than 5 wt.% Mg, some peaks of pure zinc was detected.

From the analysis of the coating layers, it can be stated that the Zn-Mg coating layers deposited by the EML-PVD shows very fine and compact crystalline structure, and they are fully and uniformly alloyed without any segregation of an element.

3.3 Corrosion resistance of the Zn-Mg coating layers

The corrosion resistance of the Zn-Mg alloy coated steels was evaluated by salt spray test. In Photo 7, corrosion resistance of unpainted panel and drawn cups were compared with reference samples of an electro-galvanized (EG) and hot-dip galvanized (GI) steel sheets. Both flat and drawn samples of Zn-Mg coated steel sheets show superior resistance to the reference samples.

In Photo 8, the corrosion resistance after electro-painting was also compared with reference samples. The blister width of Zn-Mg coated steel sheet was very low compared to the reference samples, indicating the formation of very stable corrosion products.

More investigations on overall quality performances are in progress, with the majority of them exhibiting high possibility for the application of Zn-Mg coated steel sheets for automotive, electrical appliances and construction.

4. Summary

Basic characteristics of simultaneous co-deposition of Zn-Mg coating layers by the EML-PVD technology were investigated in pilot plant scale. It was confirmed that the co-deposition of zinc and magnesium, which have quite difference of vapor pressure with each other, was possible with the aid of the induced electro-magnetic agitation effect provided by high frequency inductor. The superior corrosion resistance found from the Zn-Mg alloy coated steel offers opportunities for material for automotive, electrical appliances, and construction applications.

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