

Anti-Corrosion Performance and Applications of PosMAC[®] Steel

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PosMAC[®] is a brand of Zn-Mg-Al hot-dip coated steel sheet developed by POSCO. PosMAC[®] can form dense surface oxides in corrosive environments, providing advanced corrosion resistance compared to traditional Zn coatings such as GI and GA. PosMAC[®] 3.0 is available for construction and solar energy systems in severe outdoor environments. PosMAC[®] 1.5 has better surface quality. It is suitable for automotive and home appliances. Compared to GI and GA, PosMAC[®] shows significantly less weight reduction due to corrosion, even with a lower coating thickness. Thin coating of PosMAC[®] provides advanced quality and productivity in arc welding applications due to its less generation of Zn fume and spatters. In repeated friction tests, PosMAC[®] showed lower surface friction coefficient than conventional coatings such as GA, GI, and lubricant film coated GA. Industrial demand for PosMAC[®] steel is expected to increase in the near future due to benefits of anti-corrosion and robust application performance of PosMAC[®] steel.

Keywords: Anti-corrosion, Zn-Mg-Al alloy coating, PosMAC[®] 1.5, PosMAC[®] 3.0

1. Introduction

The manufacturing concept for the hot dip Zn-Mg-Al alloyed coating has been noticed since early 1960s with its advanced anti-corrosion property [1-3]. However, industrialization of this coating had been delayed due to its difficulties in control of Mg and Al in Zn pot. The commercialization of Zn-Mg-Al coated steels started late 1990s and early 2000s with ZAM[®] (Zn-3%Mg-6%Al, hereafter % means wt%) and SuperDyma[®] (Zn-3%Mg-11%Al) [4,5] as usage for construction materials.

Since mid 2000s, European steel makers developed Zn-Mg-Al coated steels with 1~2%Mg and 1~3%Al in the coating. This coating group has been targeted for mainly automotive applications to improve surface quality and weldability by optimizing its composition and process control [6-8]. Despite its anti-corrosion merits, worldwide spread of Zn-Mg-Al coatings has been restricted due to its limited global supply chains. POSCO has produced PosMAC[®] 3.0 coated steel in Korea since 2012 as the first Zn-Mg-Al coated steels outside of Japan and Europe

[9,10]. It is suitable for the construction and solar energy systems to increase outdoor service life [11]. Thereafter PosMAC[®] 1.5 is developed with lower Mg and Al contents to increase surface quality for other various applications in automotive and home appliances [9,12].

Since then, more steel makers in Asia commercialized the Zn-Mg-Al coated steels. The industrial specifications such as ASTM has revised for various coating compositions [13]. It is expected that global consumption of Zn-Mg-Al coated steel would increase remarkably with the expansion of suppliers and its successful application cases in various industries. Surface quality of Zn-Mg-Al coating is one of key issues in its applications in automotive and home appliances. Generally, the control of surface quality is more difficult compared to conventional GI or GA coating. This is because there is more skimming dross on the Zn pot that is easy to contaminate the coating surface. In addition, complex heterogeneous solidifications such as Zn, binary (Zn-MgZn₂), ternary (Zn-Al-MgZn₂) phases during cooling makes surface quality difficult to control.

In this study, it is surveyed the study of Zn-Mg-Al coated steel and various application properties of PosMAC[®] in anti-corrosion, arc welding and surface friction tests. Solidification process of Zn-Mg-Al coating was studied by using in-situ XRD and with thermodynamic calcu-

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lations using FactSage7.3 software. Corrosion tests were carried out in various conditions for PosMAC[®] 1.5 and 3.0 in comparison to the conventional GI and GA steels. For more practical evaluation, artificial damage, such as cut edge, molding, and scratches, was applied to the corrosion test samples.

2. Experimental Methods

2.1 Solidification Study

In this study, we investigated the high temperature phase transformations of Zn-Mg-Al coatings by using in-situ synchrotron XRD during thermal treatment [5,14]. The in-situ XRD measurement at high temperatures was performed at the 8D beamline at the Pohang Light Source. The incident X-rays were vertically collimated by a collimating mirror, and monochromatized to the wavelength of 0.6148 Å with a narrow band pass of $\Delta\lambda/\lambda = 10^{-4}$ by a double-crystal Si(111) monochromator. The focused and monochromatic X-ray beam irradiated the sample at a fixed incident angle of 12°. The diffracted X-rays at various 2θ positions were monitored using a 64 mm-long photodiode array covering 2θ angles between 14° and 40°. Test samples are ZnMgAl coated steel produced in a laboratory. The coating compositions are Zn-3%Mg-2.5%Al and Zn-1.2%Mg-1.2%Al. The coating weight is about 40 g/m² per side. The samples are heated up to 430 °C and keep it 60 sec. and cooled it to room temperature. The tests carried out in a chamber filled with He gas to avoid oxidation. Phase transformation in the coating is measured along the heat cycles. The heating rate is 5.3 °C/s and the cooling rate is to 2.1 °C/s.

2.2 Corrosion Test

To evaluate various application properties of PosMAC[®] steel, corrosion, arc welding, and surface friction were tested in various test conditions. Conventional GI and GA steels used as reference test samples. PosMAC1.5[®] and PosMAC3.0[®] are prepared with coating weight of 30 g ~ 110 g (in this paper coating weight g means g/m² per one side of the strip). The Mg contents in the coating of PosMAC1.5[®] is 1~2% and in the PosMAC3.0[®] is around 3%. Painted samples are prepared by pre-painted steel sheets (PCMs) and electro deposit (ED) coating. Artificial damages such as cut edge, surface scratch, formation, welding are imposed some of samples. Corrosion test carried out in salt spray test (SST) by ISO9227 [15] and in cyclic corrosion test (CCT) by ISO 14993 [16] and GMW14872 [17].

2.3 Arc welding

Gas metal arc welding(GMAW) test is carried out for

the purpose of chassis manufacturing for PosMAC[®] 1.5 and GI steels. Tested steel grades are YS (Yield Strength) 340 MPa and YS 420 MPa. PosMAC[®] 1.5 35g and GI 60 g are prepared on the steels. Arc welding test condition is as follows. Arc current range is 100 ~ 220 A with 14 ~ 20 V, welding speed is 55 ~ 140 cm/min. Heat input is 1.8 ~ 2.2 KJ/cm. Ar+CO₂ gas used as a shielding gas. After the test, defects in the welding beads are examined by X-ray nondestructive inspection. The weld finished parts are prepared by ED paint and then corrosion tested by GMW14872.

2.4 Friction Test

A repeated surface friction tests are carried out to evaluate friction coefficient of PosMAC[®] steel in compare to conventional GI, GA and lubricant film coated GA steels. The surface friction property is closely related with press forming quality for complex shaped parts. The test procedure is as follow. The test apparatus composed with 3 friction tips which located evenly in the circle of 200 mm diameter. Each tips surface dimension is 18 × 28 mm, and its surface is prepared by hard chromium coating and then finished by grinding. The surface hardness of the tip is 700 ~ 1,000 Hv. Friction tips contact on samples with 5 MPa compressive loads and then samples turned round repeatedly. The value of friction coefficient is continuously measured with the rotation of samples. The total rotation is 40 ~ 100 rounds. The samples surface roughness is 1.0 ~ 1.5 Ra, and test under the same oiled conditions on the surface.

3. Results

3.1 Phase formation in the coating

Melting and solidification temperatures of coatings are measured by an in-situ XRD apparatus with a heating controlled chamber. The coating is completely melted out when it is heated up to 430 °C. During the heating, Zn-3%Mg-2.5%Al coating follows melting process as follows: Al melted at 329 °C → A portion of MgZn₂ transforms to Mg₂Zn₁₁ at 342 °C → remained MgZn₂ and Zn melted at 368 °C → Mg₂Zn₁₁ melted at 377 °C. In the cooling process, it follows: solidification of binary phase (Zn-MgZn₂) at 343 ~ 334 °C. During the heating of Zn-1.2wt%Mg-1.2wt%Al coating, it follows: A portion of MgZn₂ transforms to Mg₂Zn₁₁ at 360 °C → remained MgZn₂ and Mg₂Zn₁₁ melted at 387 °C → Zn melting at 413 °C. In the cooling, it follows: solidification of Zn at 393 °C → solidification of binary phase (Zn-MgZn₂) at 347 °C. The solidification process is also calculated by using FactSage program package. Experimental data and

Table 1 Solidification behaviors of Zn-Mg-Al coatings during cooling, as measured by in-situ XRD and calculated using FactSage. Calculation results are shown in parenthesis

Coating composition	Temperature for phase formation(°C)		
	Zn primary formation	Binary phase (Zn-MgZn ₂) formation	
		Initiation	Finalization
Zn-3.0%Mg-2.5%Al	-	343 (349)	334 (341)
Zn-1.2%Mg-1.2%Al	393 (390)	347 (351)	- (341)

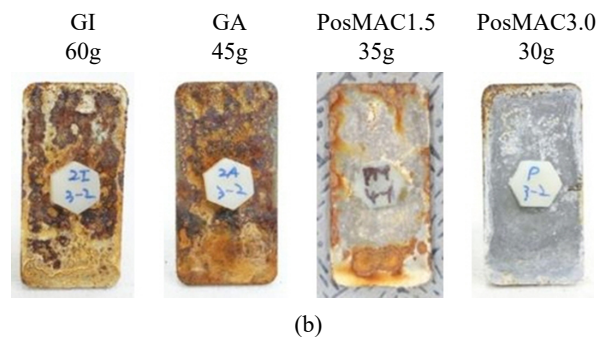
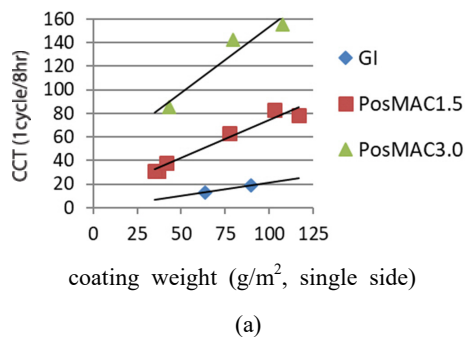
calculation results are compared in Table1. There are deviations between experiments and calculations about 6 °C. These differences are considered due to the super cooling and/or measurement errors.

3.2 Corrosion tests

Anti-corrosion performance of steels is evaluated with various test methods followed by national industrial standards or OEMs's such as ISO, ASTM, VDA, GMW, LGE etc [12]. Fig. 1 shows selected cyclic corrosion test (CCT) results by ISO14993. Fig. 1a represent test cycles of red rust generation for the GI, PosMAC® 1.5 and 3.0 with coating weight 30~120g per single side of the sample. PosMAC® 1.5 shows 4.2 times and PosMAC® 3.0 shows 9.2 times longer than GI in their red rust generation. In all the test cases, the red rust appeared to be delayed in proportion to the increase of coating weight. Fig. 1b shows appearance of GI 60g, GA 45g, PosMAC® 1.5 35g, PosMAC® 3.0 30g after 24cycle by GMW 14872. Red rust covers most of the surface on the GI and GA samples, however only partial red rust appears on PosMAC® 1.5 even though lower coating weight. PosMAC® 3.0 appears the least red rusts on the surface. Additionally, weight

loss of the samples measured after 68 cycle by GMW14872. In compare to GI, PosMAC® 1.5 appears 40% less and PosMAC® 3.0 appears 50% less in the weight loss by corrosion consumption.

Painting is applied to many parts for surface protection and decorative purposes. PCM coils are widely used in construction and home appliances, and electro-deposit painting is also used for automotive and home appliance parts. Weak points of the painted parts, especially in the case of PCM coating, in corrosion attacks are usually found in the surface damaged area such as cut edge, scratches from forming. Corrosion attacks begin in these incomplete positions from damage. To evaluate corrosion behavior in damaged cases, PCM coating prepared on GI 110g and PosMAC® 1.5 60~90g and then imposed damages such as cut edge, deep drawing, surface cuttings. These samples tested in SST for 72 ~ 720 hrs and examined rust generation and paint degradations as shown in Fig. 2. Corrosion penetrates into the interface between paint and metal coating. Although the coating weight is greater than the PosMAC® 1.5, however the GI sample causes more severe rust and paint damage. PosMAC® 1.5 shows that paint deterioration has been delayed due to



(a) Red rust generation cycles in CCT (ISO 14993) for GI, PosMAC® 1.5 and PosMAC® 3.0 with various coating weights (per single side), (b) Appearance after 24 cycles in CCT (GMW 14872) for GI, GA, PosMAC® 1.5 and PosMAC® 3.0 with various coating weights (per single side).

Fig. 1 Cyclic corrosion test for GI , PosMAC® 1.5 and PosMAC® 3.0.

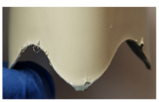
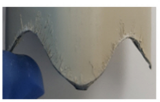
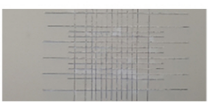


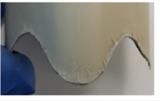



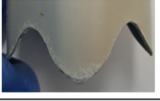

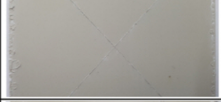

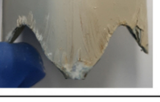


samples	Coat weight	Drawing cup		Cross cut	X cut
		SST 72 hr	SST 720hr	SST 480hr	SST 480hr
PosMAC1.5	60g				
	75g				
	90g				
GI	110g				

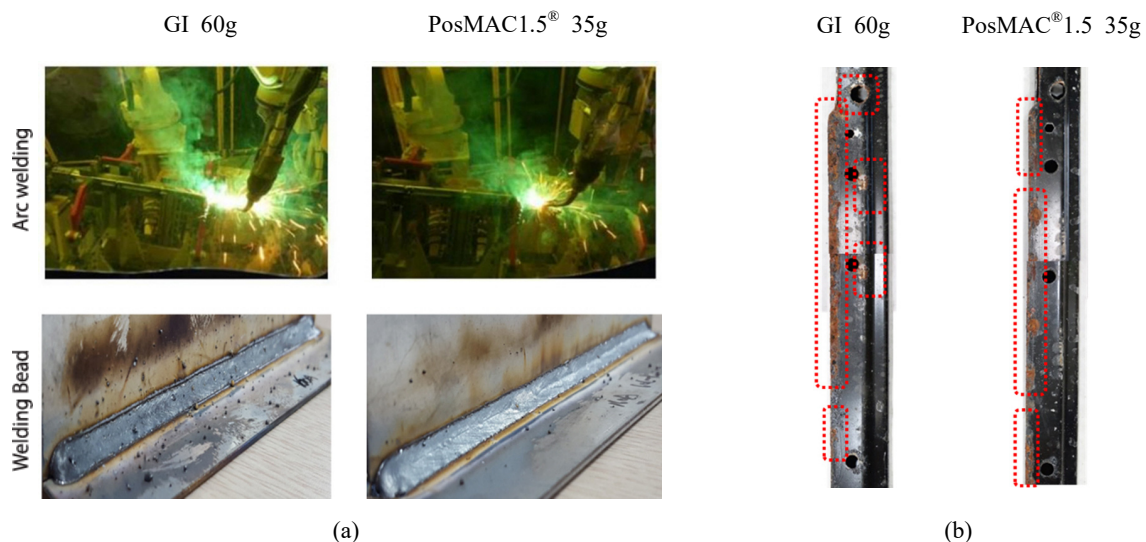
Fig. 2 Corrosion resistance in various damaged area of PCM GI 110g and PosMAC[®] 1.5 60~90g (per single side).

the slow growth of corrosion products in interface. The corrosion resistance of PosMAC[®] 1.5 improves with increase of coating weights. Previous studies [9,10,12] verified that PosMAC[®] steel has at least twice the corrosion resistance than GI, GA steels in various corrosion cycle conditions and sample conditions such as welding, molding and cutting etc. From these results, PosMAC[®] has been applied in many industrial products that demand higher reliability in corrosion protection. It can also be applied as a paint-saving solution to reduce the thickness of painting or PCM can be used as a replacement for electro-deposit painting due to its enhanced corrosion

protection.

3.3 Arc welding

Arc welding is widely used for joining of many construction structures and chassis in automotive etc. Arc welding for Zn coated steel causes severe quality problems, such as scattering of spatters, holes inside weld bead due to the Zn evaporation during Arc heating. Usually, the solution to reduce weld defects is to reduce weld speed, but it causes low productivity. To minimize welding defects with maximum productivity is the key issues in the arc welding process. PosMAC[®] could be available



(a) Zn evaporation during welding and welding bead after welding, (b) CCT 95 cycles for the chassis with GMW14872.

Fig. 3 Arc welding process and corrosion test for the chassis of GI60g and PosMAC[®] 1.5.

Table 2 Arc welding results for GI 60g and PosMAC[®] 1.5 35g

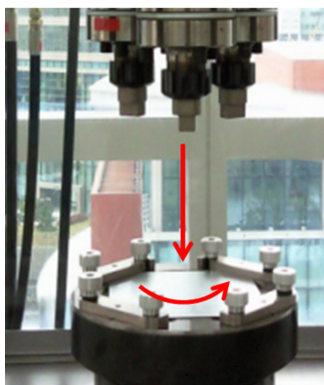
Coatings	Welding speed	Currents	Spatters	Remarks
GI (60g)	45 cm/min	113~120A	Much	-
PosMAC [®] 1.5 (35g)	60 cm/min	120~150A	Less	30% speed up

as thinner coatings due to its excellent anti-corrosion. The light coating weights would reduce the problems that come from Zn evaporation. PosMAC[®] 1.5 tested for the chassis manufacturing in comparison to GI steel. Base metal is 1.5t mm thick steel of YS 320 MPa and YS 420 MPa grades. PosMAC[®] 1.5 35g and GI 60g prepared on the strip. Fig. 3a shows welding scenes and welded part of PosMAC[®] 1.5 and GI steels. The amount of Zn fume evaporate during the arc welding and scattered spatters remains near the welded area on the parts. In case of PosMAC[®] 1.5 shows less Zn fumes and contaminations of spatters due to its thin coating layers. Optimized working conditions found through various tests as shown in Table 2. Arc welding productivity could increase up to 30% with the use of PosMAC[®] 1.5 due to its less generation of Zn fume and spatters. Weld beads were examined with X-ray inspection. PosMAC[®] 1.5 showed the same or higher quality compared to GI, although it was performed at a higher weld speed. In general, welded area is vulnerable to corrosion attacks. This is because coating layers lost or damaged by arc heating and the formation of slag intrusions on the bead's surface which would impede paint adhesions. The welded chassis parts tested for CCT by GMW14872. Fig. 3b shows test results after CCT 95 cycle. Red rust appears majorly on the welded area on both parts. However, although the coating weight has been reduced by 40%, there is relatively less rust on the PosMAC[®] 1.5 based chassis parts compared to GI. These

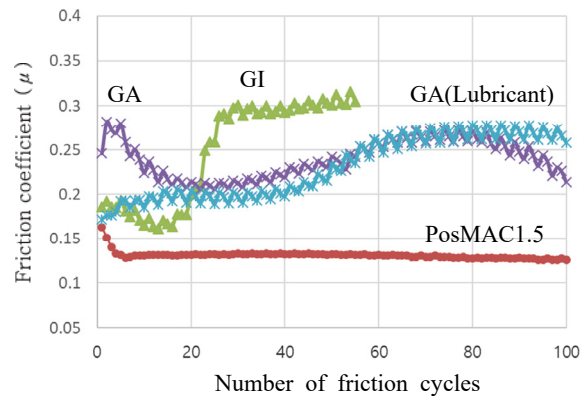
test results indicate that PosMAC[®] 1.5 has advanced anti-corrosion performance in the arc welding application. It has also verified that PosMAC[®] 3.0 shows advanced arc welding performance with its thinner coating applications.

3.4 Surface friction

Surface friction of the steel sheets is a very important for the press forming operation. The galling problem would have more occurred in press works when friction coefficient is higher. Higher friction resistance promotes surface deformation and dropping out of small particles from the surfaces and then accumulate on the tool surface with repeated working, which would make galling defects during pressing operation. Conventional Zn coatings such as GI and GA are apt to develop gallings due to their higher friction coefficient and the falling of particles from the coatings. A higher frequency of gallings would cause lower productivity because it needs interruption for press tool cleaning during production. Coating material with a lower friction coefficient and higher resistance of surface formation is a very desirable property for the pressing works. PosMAC[®] 1.5 was tested in its surface friction properties with GI, GA and GA lubricant film coated samples. As shown in Fig. 4a, friction tips contact on samples with 5MPa compressive loads and then samples turned round 100 times. The continuous change of friction coefficients was recorded with repetition in Fig. 4b. Initial friction coefficient of GI is 0.2 and it is rapidly



(a)



(b)

Fig. 4 Friction tool repetition tester (a) and variation of friction coefficient for GI, GA, GA(lubricant) and PosMAC[®] 1.5 (b).

increased when friction repetition over 20 times. It is considered that GI coating would be easily deformed due to its ductile property, and crushed particles of the coating attached on the tool surface, which rise up friction resistance. In the case of GA, there is no rapid increase in the coefficients, but it is over 0.2 during the tests. In case of lubricant treated GA, initially 0.17 however its lubricant effects disappeared after 40 times repetition and then over 0.2. In PosMAC's case, initially 0.17 and then decreased about 0.13 and maintains this value until the end of the test. Surface roughness of samples were measured before and after the test to investigate surface deformation as shown in Table 3. It measured surface roughness (Ra[um]) and peak count per 10 mm (Rpc). After the test, the value of roughness decreased due to the flat deformation of the samples. GI, GA and lubricant GA shows decrease about 50% for Ra and Rpc. This changes indicates that surface become more flat with the process of surface friction. During this process, some of crushed particles drop out from the surface and then attached on the tool surface. In case of PosMAC[®] 1.5, however, Ra and Ppc is decreased 18.9% and 13.7%. It is considered that surface morphology of PosMAC[®] becomes smooth without increase of friction coefficient as shown in Fig. 4. This surface property comes from higher hardness and toughness of the PosMAC[®] coatings. This suggests that surface morphology of PosMAC[®] settled stable form and then maintains with low level of friction resistance. Separate experiments with PosMAC[®] 3.0 were also carried out and it also show similar surface friction characteristics. The PosMAC[®] steel is suitable for com-

plex forming parts with less galling due to this low friction resistance properties.

4. Discussion

4.1 Phase study for ZnMgAl coating

Zn pot for GI coating consists of Zinc with 0.1~0.3% Al. Al reacts with the steel substrate to form a thin Fe_2Al_5 inhibition layer about 100 nm thick on the steel surface. The solidification behavior of this coating follows very similar to pure Zinc. On the contrary, higher contents of Al and Mg would promote the formation of complex phases with different solidification temperatures. Primary solidification and eutectic reactions of binary phase (Zn-MgZn₂) and ternary phase (Zn-MgZn₂-Al) occur during cooling. Solidification behaviors could be explained by analytical study of phase diagram for Zn-Mg-Al alloy system as shown in Fig. 5. Fig. 5a shows several compositions of Zn-Mg-Al coatings on the ternary phase diagram. It is understood that the kinds of phases and their ratios depend on the Mg and Al contents. Fig. 5b shows solidification behaviors from liquid to solid during 460 °C to 320 °C for GI and several of Zn-Mg-Al compositions. Change of slope of the line indicate that different phases are forming during cooling. It shows that the solidification of GI (Zn-0.2%Al) begins at 418 °C and completed soon. However, Zn-Mg-Al coating has wider solidification temperature ranges and it depends on composition of the coating. The solidification range for Zn-3%Mg-2.5%Al is 18 °C, while Zn-3%Mg-11%Al is 83 °C. The wide range of solidification temperature and its complex phase for-

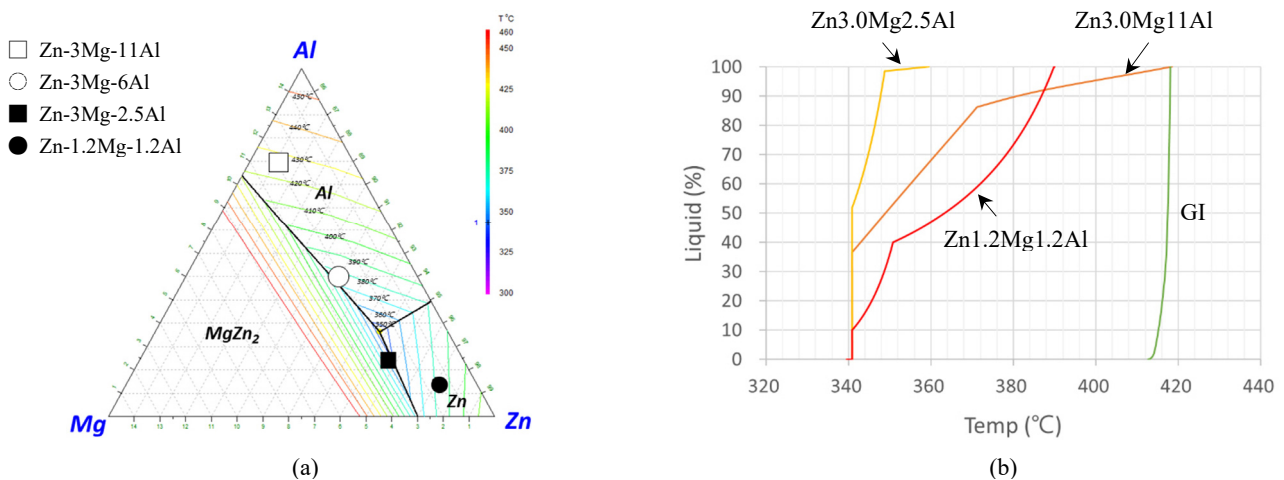


Fig. 5 Phase diagram and solidification behaviors of various Zn, Mg, Al compositions.

mations would tend to cause surface defects in the Zn-Mg-Al coatings.

4.2 Corrosion behaviors

The advanced anti-corrosion of PosMAC® comes from the compact corrosion products on the coating surface in compare to conventional Zn coating such as GI, GA and EG. The barrier properties of corrosion products on the coating surface is very important in anti-corrosion performance. In general, the compact oxide layer covered on the metal surface acts as a diffusion barrier between the corrosion environment and the metal substrates, delaying corrosion progress. Fig. 6a shows schematic mechanism of PosMAC®'s anti-corrosion by the formation of dense corrosion products which called simonkolleite and layered double hydroxide (LDH) on the surface. In case of conventional Zn coating, hydro-oxide (Zn(OH)_2) mainly forms on the surface. On the other hand, PosMAC® significantly increases service life of the coating by forming a more compact simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$) on the surface by the interaction of Mg in a corrosive environment. Al in the coating also acts as the formation of a dense LDH layer in the coating, which has an additional positive effect on corrosion protection [18]. Fig. 6b shows the appearance of test samples and magnified images of GI and PosMAC® by scanning electron microscopy (SEM) after salt spray test (SST) for 110 hours. As shown in this figure, the GI steels have porous oxides and partially red rust on the surface, indicating loss of protection by coating. However, in the case of PosMAC®, the compact oxide of simonkolleite covers the surface and inhibits corrosion progress

The advanced anti corrosion mechanism of Zn-Mg-Al

coating has been studied [19-23] and it is summarized as below. Zn reacts with oxygen in the absence of water to form a ZnO layer on the surface. In the presence of moisture (slat spray), Zn reacts with water to form Zn(OH)_2 and often the final corrosion product as hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) with the reaction of CO_2 in the air [19-21]. During the initial corrosion phase, a mixture of various corrosion products may be formed; ZnO, Zn(OH)_2 , and $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. In presence of salt, Na^+ (cations) and Cl^- (anions) migrate towards cathodic and Zn dissolution sites, respectively. In the condition of increased chloride activities and with appropriate pH value, ZnO is formed in the cathodic areas and simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$) is formed in the anodic area [19-22]. Simonkolleite would form dense thin layer on the surface and suppress the further corrosion progress. Simonkolleite is stable at pH 6 ~ 8, however, due to the increase of OH^- during corrosion process which would lift up pH, as a result, decomposes simonkolleite into ZnO or Zn(OH)_2 , which loses its anti-corrosion performance. Mg in the coating would stabilize simonkolleite by suppress the rise of pH in the environment. This is because Mg is easier to ionize than other elements, and pH remains in the stable range, as Mg^+ preferentially flow out and consumed OH^- to form Mg(OH)_2 [18,22,23]. Al in the coating would ionized to Al^{3+} , then forms compact oxide layer as layered double hydroxide (LDH) and contribute the anti-corrosion performance. LDH could be composed as ZnAl-LDH ($\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$) and MgAl-LDH ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$). The presence of Mg^{2+} could promote the early formation of LDH. Moreover, lower solubility of MgAl-LDH contribute to formation of smaller nano-sized crystal structure which would have the better barrier properties [18].

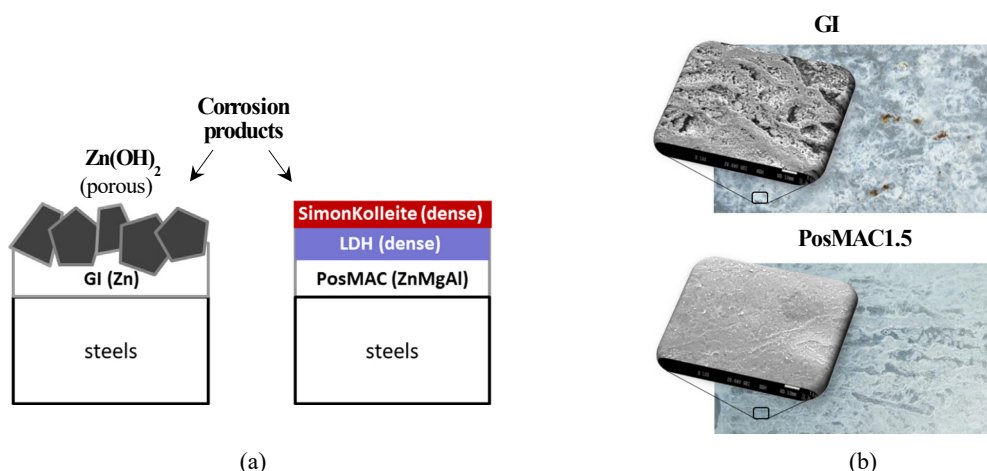


Fig. 6 Anti-corrosion performance of PosMAC® steel. (a) Schematic of anti-corrosion mechanism, (b) Surface appearance & SEM images after Salt Spray Test(SST) for 110 hr.

5. Conclusions

PosMAC[®] is Zn-Mg-Al coated steel improves corrosion resistance even with thin coating thickness. Thin coating of PosMAC[®] provides advanced quality and productivity in arc welding applications due to reduced Zn fume and spatters during heating. And its lower surface friction properties would provide great advantages to the formation of complex parts. Eventually these features would save Zn resources and also reduce energy consumption and CO₂ emission in the manufacturing industries. Application test results in this study summarized as below.

- (1) PosMAC[®] steel shows 4 ~ 9 times higher anti-corrosion performance in compare to conventional GI and GA steels in SST. Deformed PosMAC[®] steel parts also shows excellent anti-corrosion performance for both bare and painted cases.
- (2) In the application of Arc welding for chassis, PosMAC[®] 1.5 shows same or above welding quality in compare to GI due to its reduced coating weight. In the CCT corrosion test for final chassis components, PosMAC[®] 1.5 shows better corrosion resistance even though the coating weight is 40% lower than GI.
- (3) PosMAC[®] 1.5 maintains a lower friction coefficient compared to GI, GA and lubricanted GA during repeated surface friction test. After the friction test, the conventional Zn coating was in a flat abraded surface, while PosMAC[®] 1.5 maintains a stable form to appropriate for low friction resistance.

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