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EFFECT OF ATMOSPHERIC-PRESSURE GAS-PLASMA TREATMENT ON SURFACE PROPERTIES OF HOT-DIP Zn-Mg-Al ALLOY-COATED STEEL

The effect of plasma-radical change on the surface properties of Zn-Mg-Al ternary-alloy-coated steel sheets during atmospheric-pressure (AP) plasma treatment using different process gases: O₂, N₂, and compressed air was investigated. The plasma-induced radicals promoted the formation of chemical particles on the surface of the Zn-Mg-Al coating, thereby increasing the surface roughness. The surface energy was calculated using the Owen-Wendtgeometric equation. Contact angle measurements indicated that the surface free energy of the alloy sheets increased upon AP plasma treatment. The surface properties of the Zn-Mg-Al coating changed more significantly in the order air > O₂ > N₂ gas, indicating that the plasma radicals facilitated the carbonization and hydroxylation of the Mg and Al components during the AP plasma treatment.

Keywords: plasma treatment; Zn-Mg-Al-galvanized steel; surface energy; process gas

1. Introduction

Hot-dip Zn-galvanized steel sheets are widely used in various industrial applications, such as building construction and automotive panels, because of their high corrosion resistance owing to the sacrificial protection of Zn, which possesses relatively low corrosion potential as compared to Fe [1,2]. Many studies have been conducted for further improving their corrosion resistance by alloying Mg and Al with Zn to meet industrial demands and reduce the Zn-resource consumption [3-6]. The Mg and Al components in the coating layer dissolve in corrosive environments to promote the formation of compact and dense corrosion products, such as simonkolleite (Zn₅OH₈Cl₂H₂O) and layered double hydroxides, thereby significantly enhancing the barrier effect [7-9]. In addition to optimizing the alloying composition, various surface-treatment methods, such as conversion coating [10,11], chemical treatment [12], and plasma treatment [13,14], which utilize the electrochemically active characteristics of Al and Mg, have been used to improve the physical properties of the Zn-Mg-Al (ZMA) coating layer. Atmospheric pressure (AP) plasma treatment has gained immense attention because the reactive radicals in the system can be effectively used for cleaning or altering the surface roughness by modifying

the physical and/or chemical properties of material surfaces. Moreover, surface modification via an AP system is simple and cost-effective because vacuum is not required [15-17]. Although many reports are available on the AP plasma treatment of various material surfaces, only a few studies have been carried out on the AP plasma treatment of ZMA ternary-alloy-coated steel sheets. In this study, AP plasma treatment was performed on the surface of a ZMA-coated steel sheet. In particular, the process gas was changed during the plasma operation to investigate the effect of plasma-radical change on the surface properties of the ZMA coating layer.

2. Experimental

The substrates used in this study were 0.8-mm-thick ZMA alloy-coated steel sheets (POSCO Co., Ltd.). Inductively coupled plasma analysis indicated that the ZMA coating had a coating weight of 72.4 g/m² and comprised approximately of 2.93 and 2.61 wt% of Mg and Al, respectively. Prior to the plasma treatment, the samples were cut into 20 mm × 20 mm pieces and ultrasonically degreased by immersing in acetone, ethanol, and deionized water for 10 min each, followed by air blowing.

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The ZMA samples were irradiated by plasma that was continuously generated at atmospheric pressure. To investigate the effects of the plasma-radical change on the surface properties of the steel sheets, different oil-free process gases, i.e., O₂, N₂, and clean compressed air, were passed through a discharge zone wherein an arc was generated using a high-voltage power supply (Plasmacreat, FG3001). Plasma was then emitted from a jet head with a diameter of 4 mm in the form of a concentrated beam with a frequency and pressure of 21 kHz and 4 bar, respectively. The plasma jet was moved at a constant distance of 18 mm from the substrate to ensure uniform intensity. The jet head was moved horizontally at the speeds of 0.1 and 1 mm/s to observe the effect of the plasma-irradiation time on the surface properties of the samples. The surface morphologies of the samples were observed using field-emission scanning electron microscopy (FE-SEM) (SU-70, HITACHI) and atomic force microscopy (AFM) (Digital Instruments Nanoscope IV A). The chemical composition of each microstructure was determined using energy-dispersive X-ray spectroscopy (EDS). Furthermore, the contact angles of the samples were measured using a sessile-drop contact angle measurement system (Phoenix 300, SEO). Distilled water and diiodomethane solution were used for analyzing the dispersion and polarity elements of the samples, respectively. The volume of each drop was 3 μL and three drops were tested for reproducibility under each set of conditions. The surface free energy of each sample was obtained using the Owen-Wendtgeometric equation.

3. Results and discussion

Fig. 1 shows the FE-SEM images of the ZMA surface before and after the AP gas-plasma treatment with different process gases at the speed of 0.1 mm/s. Binary eutectic Zn/MgZn₂ and ternary eutectic Zn/Al/MgZn₂ structures were predominant rather than the Zn primary phase in the as-grown coating layer, as shown in Fig. 1(a) [6]. After plasma irradiation, white spherical particles were formed in all the samples, as shown

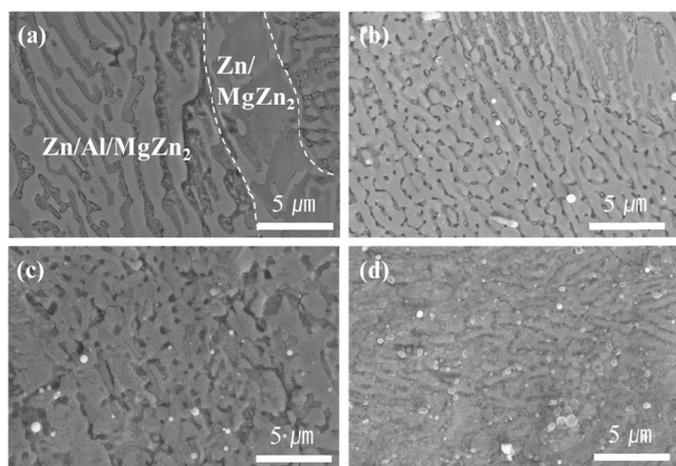


Fig. 1. FE-SEM images of the Zn-Mg-Al-coated surface (a) before and after the AP plasma treatment with different process gases: (b) N₂, (c) O₂, and (d) air

in Figs. 1(b)-1(d). The particle size and number of particles of the air and O₂-treated samples were higher than those of the N₂-treated sample. In particular, in the case of the air-treated sample, plasma-induced products other than spherical particles were observed throughout the surface, as shown in Fig. 1(d). The surface chemical compositions of the samples were analyzed using EDS and the results are summarized in TABLE 1.

TABLE 1

Chemical compositions of the Zn-Mg-Al-coated surfaces before and after the AP plasma treatment with different process gases

Sample	Chemical composition (wt%)			
	O	Mg	Al	Zn
As grown	1.63	3.25	2.80	Bal.
N ₂ -plasma-treated	2.72	3.34	3.02	
O ₂ -plasma-treated	5.70	3.41	3.12	
Air-plasma-treated	21.06	3.75	2.49	

It is noteworthy that the oxygen content of the air-plasma-treated sample, which possessed several spherical particles and other products on the surface (Fig. 1(d)), was significantly higher than those of the other samples. This suggests that the chemical-product formation was strongly affected by the radicals generated by the elements in air other than N and O, such as CO₂ and/or H₂O. Oxidation, carbonization, and hydroxylation could result in the formation of an oxide, a carbide and/or a hydroxide intermediate phase, respectively, on the surface owing to the reactions between the radicals and ZMA components during the plasma treatment with air as the process gas.

To observe the changes in the surface morphology of the ZMA coating layers, their AFM images before and after the plasma treatment with different process gases were obtained. As shown in Fig. 2, circular particles that were absent in the as-grown sample were clearly observed in the images of the

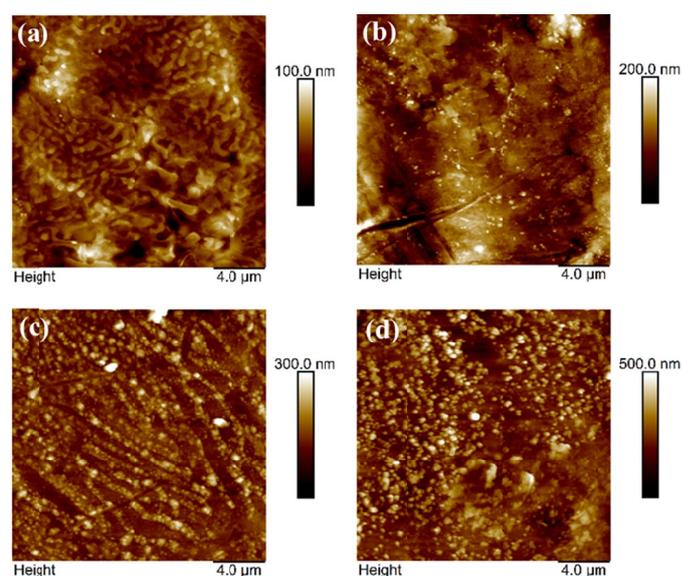


Fig. 2. AFM images of the Zn-Mg-Al-coated surface (a) before and after the AP plasma treatment with different process gases: (b) N₂, (c) O₂, and (d) air

plasma-treated samples. This is consistent with the FE-SEM observations. The RMS roughness values of the as-grown, N₂-, O₂-, and air-plasma-treated samples treated at the speed of 0.1 mm/s were 9.75, 23.4, 25.2, and 49 nm, respectively. The corresponding values for the samples treated at the speed of 1 mm/s were 9.3, 10.4, 16.4, and 21.3 nm. This indicates that the surface roughness of the samples increased with an increase in the amount of the chemical particles and products formed.

To investigate the variation in the surface energy of the samples with the change in their surface chemistry and roughness after the AP plasma treatment, the surface energy of the ZMA coating layer was calculated using the Owen-Wendtgeometric equation as follows[18].

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (1)$$

$$\gamma_L(1 + \cos\theta) = 2\{(\gamma_S^d \gamma_L^d)\}^{0.5} + \{(\gamma_S^p \gamma_L^p)\}^{0.5} \quad (2)$$

where γ_S is the surface free energy of the ZMA layer (mJ/m²) and γ_S^d and γ_S^p are the surface free energies of the solid dispersion and polarity elements, respectively. Furthermore, γ_L , γ_L^d , and γ_L^p are the surface free energy, surface free energy of the dispersion element, and surface free energy of the polarity element, respectively, of the liquid used in the contact-angle measurement. The contact angle (θ) was measured using distilled water and diiodomethane solution as the dispersion and polarity elements, respectively. In this study, we considered γ_L^d , γ_L^p , and γ_L to be 21.8, 51, and 72.8 mJ/m², respectively, for distilled water and 48.5, 2.3, and 50.8 mJ/m², respectively, for the diiodomethane solution [18].

Fig. 3 shows the contact angles of the ZMA coatings before and after the AP plasma treatment with different process gases and irradiation times, as obtained using distilled water and diiodomethane solution. The results indicated that the contact angle decreased after the AP plasma treatment, and it decreased further with an increase in the irradiation time. The surface free energy was obtained by calculating γ_S^d and γ_S^p using the values mentioned earlier and the measured contact angles, and the results are shown in Fig. 4. It is evident that the surface free energy of the coatings increased after the AP plasma treatment, and it increased further with an increase in the plasma irradiation time. Furthermore, among the plasma-treated samples, the air-plasma-treated sample exhibited the highest surface free energy. The increase in the surface free energy of the air-plasma-treated sample can be attributed to the changes in the morphology and surface chemistry of ZMA. The surface chemistry of ZMA can be altered by irradiating it with the ions and radicals generated by plasma [13,14,19]. The highly reactive radicals released from the broken bonds of elements in air react with the excited molecules and ions of the ZMA surface, resulting in the formation of various oxide, carbide, and hydroxide phases such as MgO, Al₂O₃, AlOOH, and Zn₅(CO₃)₂(OH)₆ [13,14]. Furthermore, the surface hydrophilicity of the air-plasma-treated sample was expected to increase and the surface energy of the polar elements was higher because of the removal of contaminants and the formation of functional groups, such as hydroxyl (–OH) and carboxyl

groups (–COOH or –CO₂H) [13,19,20]. Currently, research is being conducted to identify the intermediate chemical products formed on the surface of ZMA coating layers plasma-treated in the presence of different process gases.

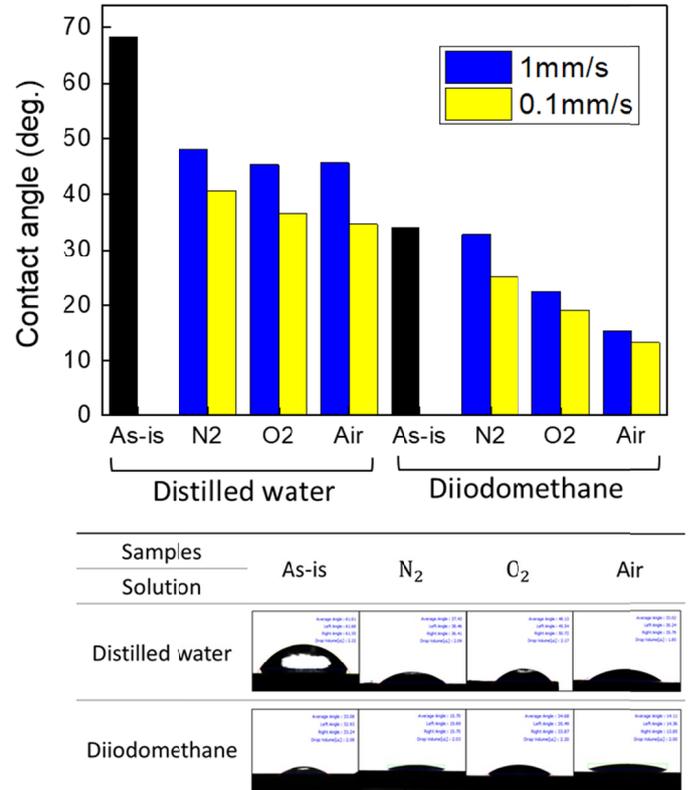


Fig. 3. Contact angles of the Zn-Mg-Al coatings before and after the AP plasma treatment with different process gases and irradiation times

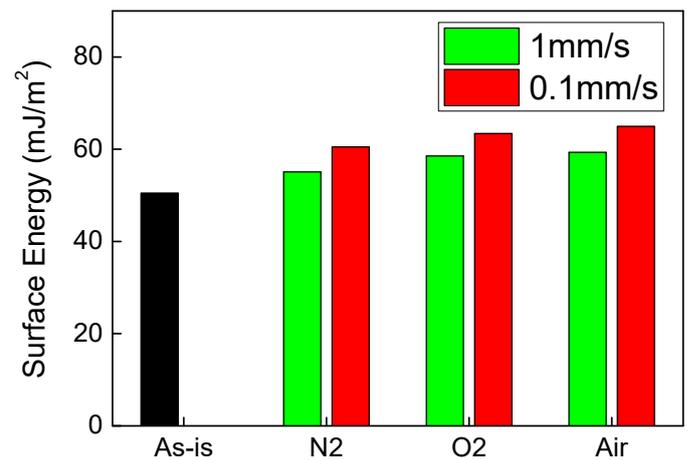


Fig. 4. Surface free energy of the Zn-Mg-Al coatings before and after the AP plasma treatment with different process gases and irradiation times

4. Conclusions

In this study, AP gas-plasma treatment was performed on the surface of Zn-Mg-Al-coated steel sheets. Different process gases, i.e., O₂, N₂, and clean compressed air, were used during the plasma operation to investigate the effect of radical changes

on the coating. Surface morphological analysis indicated that the plasma treatment induced the formation of chemical particles and products, resulting in an increase in the surface roughness of the steel sheets. The contact angle and surface free energy of the sheets decreased and increased, respectively, after the AP plasma treatment. The effect of the process gases on the surface roughness and chemistry of the Zn-Mg-Al-coated steel sheets decreased in the following order: air > O₂ > N₂ gas. Furthermore, the product formation and variation in the surface chemistry were strongly influenced by the radicals induced by the elements present in air, such as CO₂ and/or H₂O, indicating that carbonized and hydroxyl radicals facilitated the carbonization and hydroxylation of Mg and Al, respectively, during the plasma treatment of the Zn-Mg-Al alloy-coated steel sheets.

Acknowledgments

This work was supported by the [National Research Foundation of Korea (NRF)] grant funded by the Korea Government (Ministry of Science and ICT) [No. 2022R1A2C1008972]. This work was also supported by the Technology Innovation Program (20012941, 20016850) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea). This work was also supported in part by the Technology Development Program (S3160560, S3245299) funded by the Ministry of SMEs and Startups (MSS, Korea).

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