CORROSION SCIENCE AND TECHNOLOGY, Vol.23, No.4(2024), pp.289~295 pISSN 1598-6462 / eISSN 2288-6524
[Research Paper] DOI: https://doi.org/10.14773/cst.2024.23.4.289

Characteristics of Hot-Dip Znmgal Coatings with Ultra-High Corrosion Resistance

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(Received January 11, 2024; Revised June 15, 2024; Accepted June 23, 2024)

Zn-Mg-Al alloy hot-dip galvanized steel sheet has high corrosion resistance. Compared to conventional Zn coating with the same coating thickness, the high corrosion resistance Zn-Mg-Al coating is more corrosion-resistant. Various coating compositions are commercially produced and applied in diverse fields. However, these steel sheets typically contain up to 3 wt% magnesium. In recent years, there has been a growing demand for higher corrosion resistance in harsh corrosive environments. Therefore, variations in Mg and Al contents were investigated while evaluating primary properties and performance. As a result, we developed new alloy-coated steel with ultra-high corrosion resistance. A Zn-5 wt%Mg-Al coated steel sheet was evaluated for its corrosion resistance and various properties. As the amount of Mg added increased, the corrosion loss tended to decrease. The corrosion resistance of the coated steel sheet in a particular composition, the Zn-5 wt%Mg-Al coating sheet, was about 1.5 to 2 times higher than that of the conventional Zn-3 wt%Mg-Al coating sheet. Ultimately, this ultra-high corrosion-resistance coated steel sheet will provide a robust solution to conserve Zn resources and contribute to a low-carbon society.

Keywords: *Zn-Mg-Al coating, Ultra-high corrosion resistance*

1. Introduction

Galvanized steel with zinc coating have sacrificial properties where zinc with a lower oxidation-reduction potential than iron corrodes first when exposed to a corrosive environment, thereby suppressing the corrosion of steel. Additionally, when the zinc coating oxidizes, it forms a dense corrosion product on the surface of the steel, effectively blocking the steel from the oxidizing atmosphere and enhancing the internal corrosion resistance of the steel. These favorable properties have contributed to the expanded application of zinc-coated steel in recent years to construction materials, home appliances, and automotive industries.

However, due to the advancement of industries, atmospheric pollution has increased. In addition, regulatory bodies are enforcing stricter measures to conserve resources and energy. These factors have led to a growing demand for steel that possesses superior corrosion resistance compared to traditional zinc-coated steel. Consequently, researchers have been extensively exploring ways to enhance the corrosion resistance of steel. One approach that has been extensively studied involves adding elements like aluminum (Al) and magnesium (Mg) to the zinc plating bath [1-3]. This process has resulted in the production of Zn-Mg-Al alloy-coated steel, where magnesium is included in the Zn-Al plating bath composition, and has been found to enhance corrosion resistance. When exposed to the environment, the Zn-Mg-Al alloy-coated steel undergoes local or overall solidification deformation due to the oxidation reaction of Al and Mg. This microscopic solidification deformation is observed as macroscopically uneven surface morphology, which is a major cause of reduced surface quality of the steel. Moreover, Zn-Mg and Zn-Mg-Al form an oxide film such as MgO and Al_2O_3 at the

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top of the plating bath due to their high oxidizability, which creates dross defects [4-6].

Traditionally, Mg has been added to Zn-Al alloy zinc-coated steel to improve their corrosion resistance. However, excessive Mg addition resulted in frequent removal of floating drosses, which impeded the appearance quality of the product and made plating bath management difficult. Moreover, increasing the Mg content darkens the appearance of the product and makes it harder to ensure surface quality due to added surface damage factors [7,8]. Therefore, to produce highly corrosion-resistant Zn-Mg-Al alloy coated steel with Mg content higher than 3%, advanced technology in equipment conditions, process temperatures, and coating composition is necessary.

Since 2017, we have developed independent technology and new equipment for producing highly corrosion-resistant Zn-Mg-Al alloy coated steel containing 5% or more Mg. In this paper, we compare the characteristics of PosMAC® Super coated steel, which have twice the corrosion resistance of PosMAC®3.0 due to the added Mg and Al. Additionally, we discuss the potential industrial applications of this highly corrosion-resistant steel for robust applications.

2. Characteristics of PosMAC® Super

2.1 Corrosion resistance

The excellent corrosion resistance characteristic of Zn-Mg-Al alloy coated steel is mainly based on the creation of microstructures derived from the Mg component with a low electrochemical potential and rapid coverage by corrosion products with corrosion suppressive properties on the external surface. [9,10] Generally, the dense oxide structure formed on the surface acts as a barrier and obstructs the connection between the metal and the external corrosive environment, delaying corrosion.

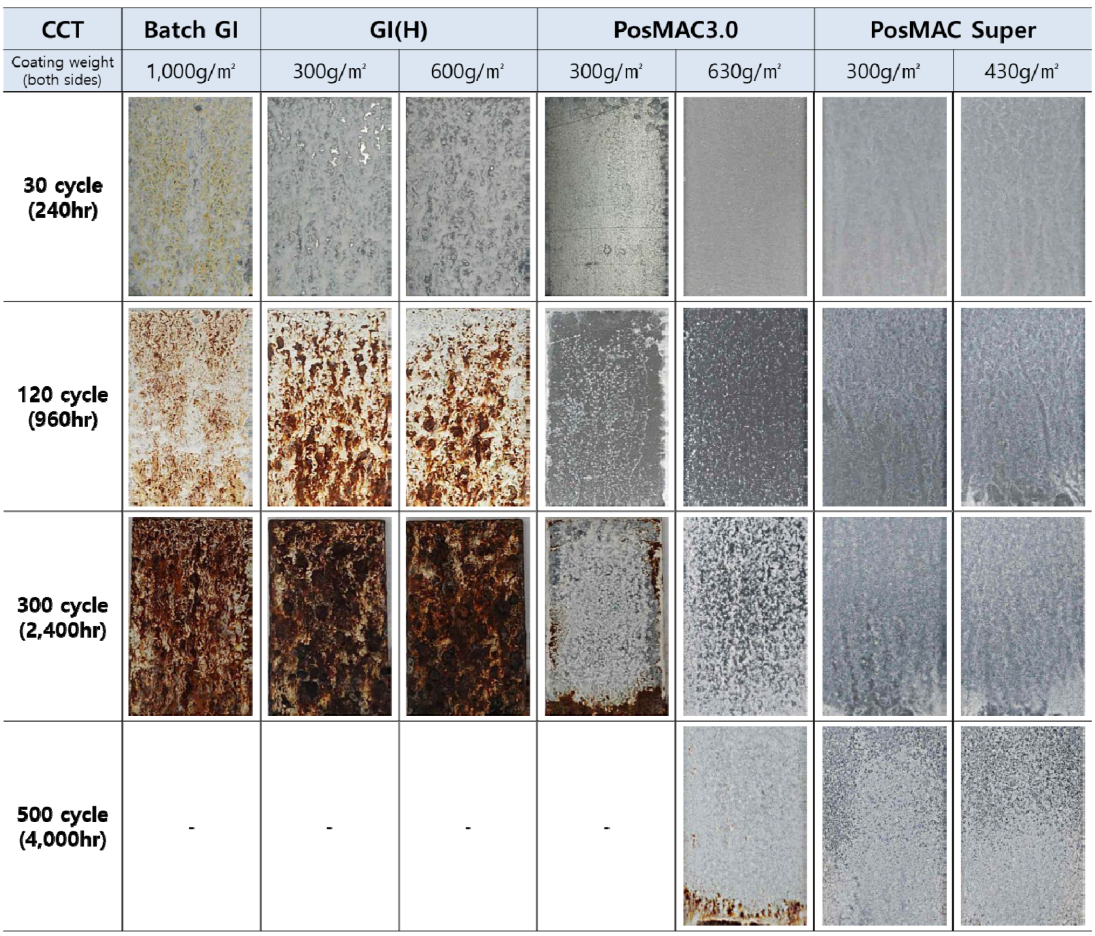

Fig. 1. Cyclic Corroion Test (CCT) results of flat surface corrosion resistance of PosMAC® Super (ISO 14933)

PosMAC® Super is a Zn-Mg-Al alloy coated steel that contains an ultra-corrosion-resistant alloy coating, which surpasses the limit of high-corrosion-resistant steel containing 3% Mg by adding 5-6% Mg. The addition of alloy elements such as Mg and Al to Zn improves the corrosion resistance of the product. However, if the Mg content is raised above a certain level, the chemical reaction increases, and the dross generation rates increase, making process control difficult and lowering the processing quality of steel, such as welding. As a result, the development of technology that simultaneously secures corrosion resistance and operating stability while increasing the Mg content and raising the Al content to 12-13% is necessary. In particular, in terms of operational stability, Al has a lower oxidation ability than Mg, so when added in a small amount, the effect of suppressing Mg oxidation is small. However, if an appropriate amount is added, dense Al_2O_3 is formed on the surface of the plating bath, making it possible to suppress Mg oxidation.

Fig. 1 shows the results of comparing and evaluating the corrosion resistance of PosMAC® Super, PosMAC®3.0, and GI materials through a Combined Cyclic Corrosion Test (CCT). The test involved spraying saltwater for 2 hours at 35 ºC and 5% NaCl, drying for 4 hours at 60 ºC and 20-30% relative humidity, and then maintaining at 95% relative humidity for 2 hours at 50 ºC in a repeated every 8 hours. The test specimens were prepared without post-treatment to attach the film, and were 13 μm thick for PosMAC® Super, 12 μm thick for PosMAC®3.0, and 25 μm thick for GI material specimens. The results indicated that the GI material exhibited red rust at the 30th cycle, while PosMAC®3.0 showed red rust at the 90th cycle.

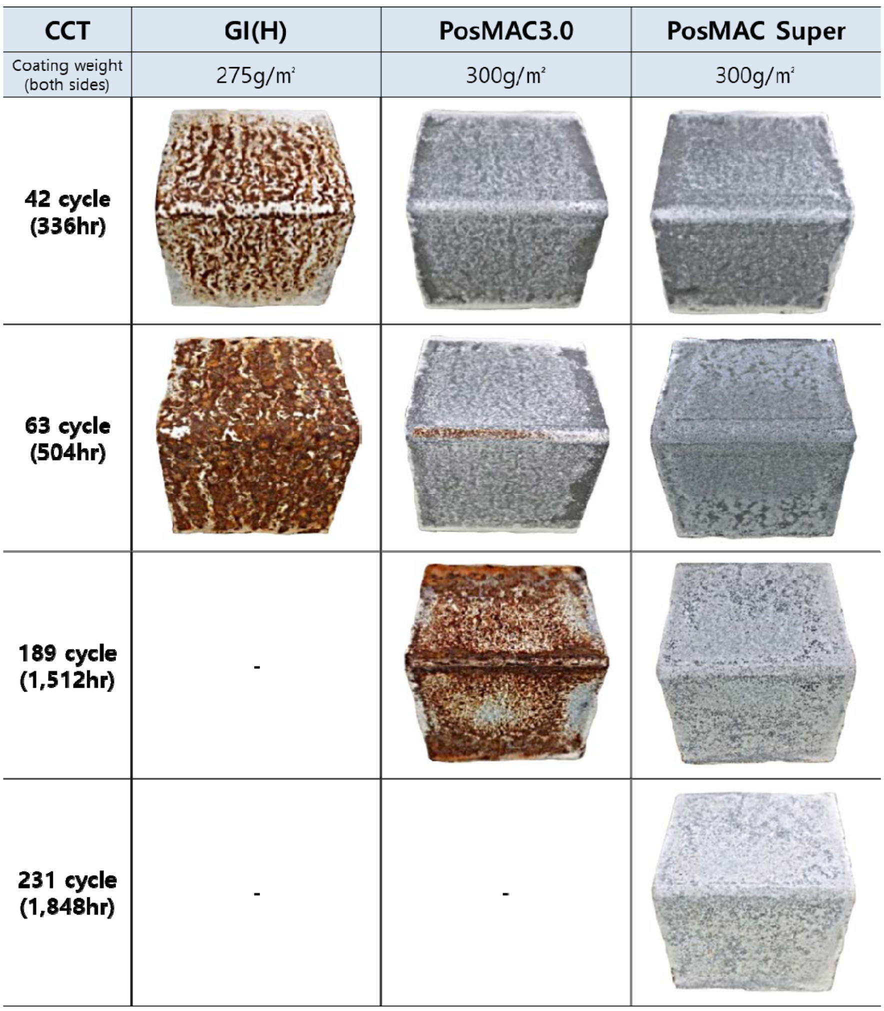

Fig. 2. Comparison of the corrosion resistance of bending processed parts after 90º bending (Radius = 0)

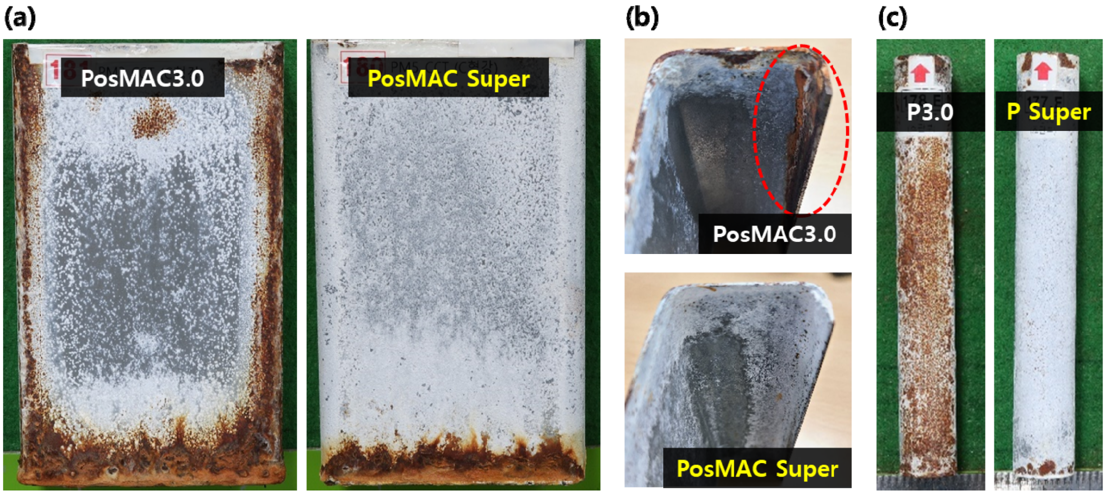

Fig. 3. Corrosion resistance comparison result of PosMAC®3.0 and PosMAC® Super (275 g/m^2) after CCT 180 cycles

Remarkably, PosMAC® Super did not experience any red rust, even after 120 cycles. Although the coated layer thickness of PosMAC® Super was approximately half that of the GI material, it demonstrated outstanding flat-surface corrosion resistance.

Fig. 2 shows the results of the combined cyclic corrosion test (CCT) of bending processed parts. It shows that the corrosion resistance of the bending processed parts of PosMAC® Super is superior to that of GI or PosMAC®3.0. This finding confirms that the corrosion resistance advantage of bending processed parts is enhanced in highly corrosion-resistant steel. This means that PosMAC® Super products exhibit over 10 times the corrosion resistance found in traditional GI products and are twice as corrosion resistant as PosMAC®3.0 products. Therefore, we can conclude that PosMAC® Super is advantageous in environments vulnerable to corrosion.

Fig. 3 shows the results of the corrosion resistance of processed practical products, focusing on C-angle pipes and pipe forming. It was confirmed that PosMAC® Super had superior corrosion resistance in processed products in comparison to PosMAC®3.0.

2.2 Chemical resistance

In general, zinc coating layers exhibit excellent corrosion resistance in pH-neutral solutions, but their corrosion resistance deteriorates in strongly acidic or alkaline environments. Therefore, it is important to examine how adding Al and Mg affects their corrosion resistance in corrosive environments and expand their applicable range. In the case of Al, when exposed to air, a layer of Al_2O_3 oxide is immediately formed on the surface, which acts as a protective film to strongly protect aluminum against corrosion. However, aluminum corrosion can occur when the Al_2O_3 film is destroyed, particularly in the presence of Cl- ions or an alkaline environment. Moreover, much of aluminum corrosion mostly occurs through localized corrosion rather than overall surface corrosion. On the other hand, Mg reacts with most acidic solutions such as dilute sulfuric acid or hydrochloric acid, resulting in the generation of hydrogen gas. And Mg has low reactivity with alkaline solutions due to the formation of insoluble magnesium hydroxide on the surface.

Fig. 4 shows the comparison of the chemical resistance of PosMAC® Super with PosMAC®3.0 and GI. The test samples of 2.0 mm thickness with a double-sided coating amount of 300 g/m^2 were prepared without post-treatment films. Fig. 4a shows the change of potential difference over time after immersion in a 5% NaCl solution. Due to the continuous activation-passivation of corrosion products in the NaCl solution, the potential of the surface where corrosion products are formed naturally increases, and the stability of the corrosion products represents the rate of increase in potential. It was confirmed that the change in the potential difference of PosMAC® Super was relatively stable compared to PosMAC®3.0 and GI. Fig. 4b shows the evaluation of corrosion reduction when immersed in a 5% NaCl solution. PosMAC® Super exhibited the lowest corrosion loss, which predicts its superior performance in seawater application. Fig. 4c shows the corrosion loss

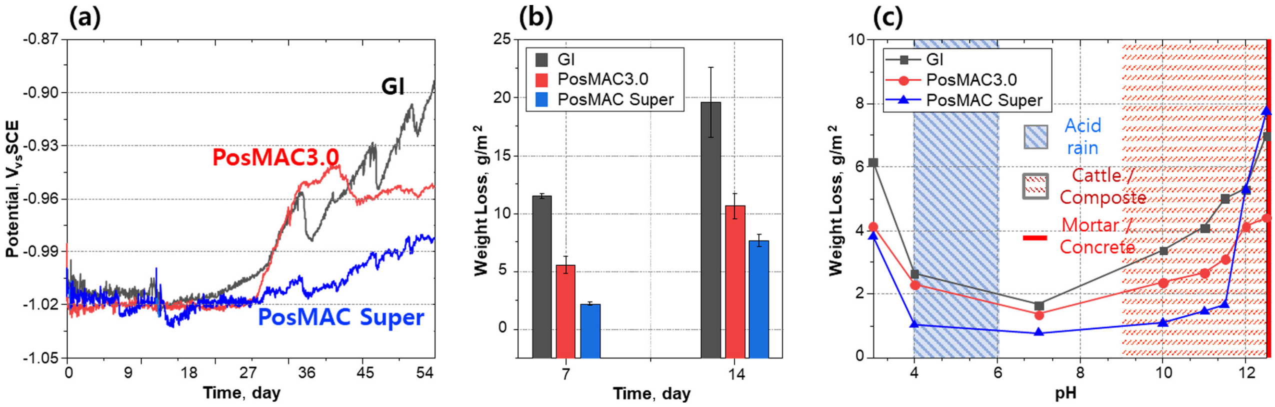

Fig. 4. Chemical resistance (a) potential difference behavior with time change when immersed in NaCl aqueous solution, (b) weight loss of corrosion reduction in NaCl aqueous solution immersion, and (c) weight loss of corrosion reduction in acid and alkali aqueous solution immersion (24 hours)

measured after immersion for 24 hours at varying pH levels by adding H_2SO_4 acid or NaOH alkaline solution to a 5% NaCl solution. It was confirmed that PosMAC® Super exhibited the least corrosion loss in not only the normal neutral environment but also in the acidic area between pH 4 and 6 and the alkaline area between pH 9.5 and 11.5. In an extremely alkaline immersion atmosphere after pH 11.5, the high content of Al in PosMAC Super is hydroxided and decomposed. However, corrosion resistance in extreme alkaline immersion atmosphere can be supplemented through post-treatment. This result suggests that PosMAC® Super is advantageous in application to factory areas or alkaline environments.

3. Resistance to Galling

Surface friction characteristics have a significant impact on surface processing, specifically in press part forming. During repetitive press processing, the residual substances detached from the galvanized steel surface by friction cause galling defects by being deposited on the press mold surface. The galling defects act as a factor that reduces productivity since the shorter the period in which galling defects occur frequently, the more often the press operation must be stopped and the mold must be ground and cleaned.

Using a circular friction tester, we evaluated the change in the friction coefficient by increasing the number of continuous friction cycles. The continuous friction coefficient was measured under the conditions of pressure of 5 MPa and speed of 200 mm/s. And the test specimen had a thickness of 2.0 mm and a double-sided plating amount of 300 g/m² without post-treatment. Fig. 5 shows that the friction coefficient of PosMAC® was smaller than

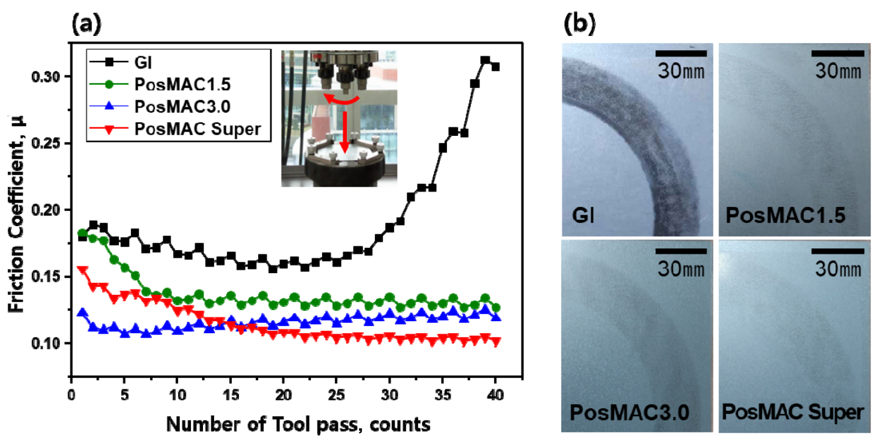

Fig. 5. (a) Continuous change of coefficient of friction, and (b) surface appearance after evaluation of anti-galling resistance

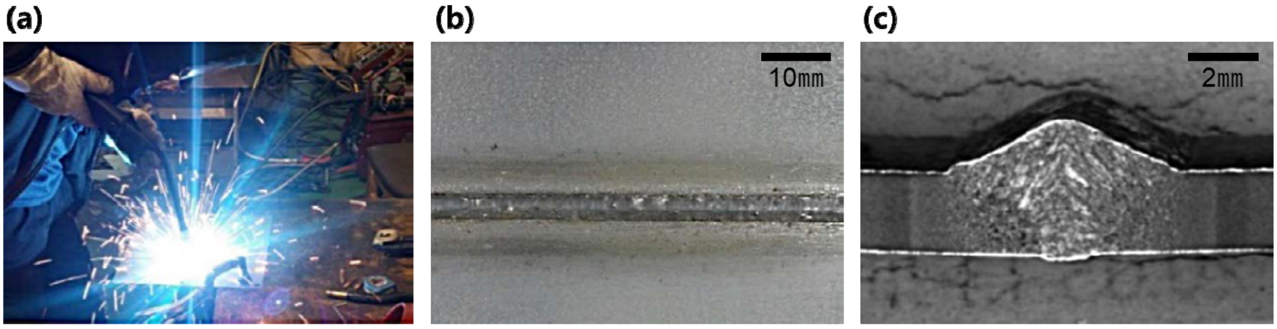

Fig. 6. Arc welding evaluation of PosMAC® Super (a) welding procedure, (b) weld bead appearance, and (c) weld bead cross section

that of GI. In the case of GI, the friction coefficient gradually increased with increasing friction cycles, while in the case of PosMAC®, there was hardly any change in the coefficient. PosMAC® have excellent galling resistance, and no peeling of the steel occurred during surface scratching or friction coefficient measurement. This means that in press operations that require heavy processing, the contamination of the mold is minimal, which can provide customers with the advantage of reducing mold cleaning costs and enhancing productivity.

The above advantages of PosMAC® can be attributed to the hardness of the plating structure, which is higher than that of GI. The measurement of micro hardness (Hv) resulted in GI showing 60 - 80 Hv, PosMAC®1.5 showing 90 ~ 110 Hv, PosMAC®3.0 showing 120 ~ 130 Hv, and PosMAC® Super showing 190 ~ 210 Hv, indicating a hard surface characteristic. This is due to the relative distribution of a significant amount of hard $MgZn_2$ on the surface of PosMAC® Super

4. ARC Weldability

Arc welding is widely used in the manufacturing of building structures and other products. When using zinc-coated materials with Arc welding, there can be quality issues such as weld porosity caused by the sudden melting and evaporation of Zn during welding and spattering of the weld pool. In this study, a PosMAC® Super sheet with a thickness of 2.0 mm and a double-sided plating amount of 300 g/m^2 was used, with a welding current of 140 ~ 150 A, a welding voltage of 21 ~ 23 V, and a welding speed of 0.6 m/min. Fig. 6 shows the test results, which indicate that the weld bead characteristics are excellent, and that a welding quality similar to that of GI and PosMAC®3.0 was achieved, ensuring the strength of the welded joint. Since the coating layer of the weld joint is destroyed, the corrosion resistance of the weld joint can be ensured through an additional coating such as Zn spray.

5. Conclusion

POSCO has succeeded in mass production of PosMAC® Super, which was developed and field-tested for practical use. PosMAC® Super is a new PosMAC® line-up of POSCO, featuring more than double the corrosion resistance due to its increased magnesium and aluminum content compared to existing products. In 2017, basic research began, including a literature review and experiments, and evaluations were conducted several times at the work site from the beginning of 2020. As a result, optimal composition and plating conditions were established, and productivity verification was completed. Existing high corrosion-resistant steel sheets have limitations when applied to facilities in high-salt and high-humidity aquatic environments or special environments such as coastal and industrial areas. However, since PosMAC® Super can overcome these limitations, it will be the leading steel product for green energy material that can respond to markets that are quickly changing towards low-carbon and eco-friendliness.

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