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ACCELERATED CORROSION BEHAVIORS OF Zn, Al AND Zn/15Al COATINGS ON A STEEL SURFACE

POSPEŠENO KOROZIJSKO OBNAŠANJE Zn, Al IN Zn/15Al PREKRITIJ NA POVRŠINI JEKLA

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Zn, Al and Zn/15Al coatings can be produced in optimum conditions by the twin wire arc (TWEA) spraying technique. The coatings are used for corrosion protection in a variety of industrial applications. In this study, the accelerated corrosion behavior of Zn, Al and Zn/15Al coatings on a steel surface during the salt-spray testing period was investigated. The surfaces of steel coupons were coated with Zn, Al and Zn/15Al using the TWEA spray-deposition system. The corrosion test was performed in a chloride atmosphere in a salt-spray test for over 2000 h. The corrosion of samples is assessed as the ratio of the corroded area of the specimens. The salt-spray test results showed that Al and Zn/15Al coatings have a better corrosion resistance than Zn coatings.

Keywords: salt spray, corrosion, coating, Zn, Al, Zn/15Al

Zn, Al in Zn/15Al prekritja lahko pripravimo v optimalnih pogojih s tehniko dvožičnega ločnega brizganja (RWEA). Prekritja se uporablja za zaščito proti koroziji pri različnih industrijskih uporabah. V tem delu smo raziskali pospešeno korozijsko obnašanje Zn, Al in Z/Al prekritij na površini jekla z metodo slanega naprševvanje. Površina vzorcev jekla je bila prekrita z Zn, Al ali Zn/Al prekritjem s TWEA sistemom depozicije. Preizkus v kloridni atmosferi in naprševanjem je trajal 2000 ur. Korozija je bila ocenjena kot delež korodirane površine vtorcev. Preizkusi so pokazali da imata večjo korozijsko obstojnost pri slanem naprševanju prekritji A in Zn/15Al kot prekritje Zn.

Ključne besede: naprševanje s slanico, korozija, prekritja Zn, Al, Zn/15Al

1 INTRODUCTION

Corrosion is one of the main causes of the degradation of metallic materials. Corrosion is the most widespread form of metal deterioration, because most metallic structures and equipment installations are exposed to natural corrosive environments. The generation of zinc (Zn) and zinc alloy coatings on steel is one of the commercially most important processing techniques used to protect steel components exposed to corrosive environments [1].

In recent decades, aluminum (Al) and zinc-aluminum (Zn-Al) alloy coatings have been used instead of zinc in certain atmospheric applications. Although these coatings have some advantages over zinc, they are not able to cathodically protect steel substrates in all types of natural atmospheres [2]. Aluminum, which can passivate both in air and when immersed in a solution, has good corrosion-resistance properties, whilst Zn can provide mainly galvanic protection for most metal substrates. A Zn–Al alloy possesses the advantages of both Al and Zn, making it a good coating material for corrosion protection [3].

The corrosion protection of Zn-coated steels arises from the barrier action of the zinc layer, the secondary barrier action of the zinc corrosion products and the cathodic protection of zinc on an unintentionally exposed part of the steel, with the coating acting as a sacrificial anode. If the exposure conditions are such that there is either depletion of air, but a high humidity or a medium containing, strongly aggressive species like chloride or sulphate ions, the Zn dissolves, forming soluble, less dense and scarcely protective corrosion products, which sometimes lead to localized corrosion. Aluminum coatings have overcome these two problems. Nevertheless, as they cannot provide cathodic protection to exposed steel in most environments, early rusting occurs at the coating defects and cut edges. In addition, these coatings are also subjected to crevice corrosion in marine environments. For years, many attempts to improve the corrosion resistance of zinc and aluminum coatings through alloying such as Zn/Al 85/15 were carried out [4,5].

Thermal spray coatings have been used for over 50 years in industries for a variety of applications. The TWEA spraying process is a very suitable method for metallic coatings. Aluminum and zinc aluminum coatings are extensively used for the corrosion protection of iron and steel in a wide range of environments and have been shown to provide long-term protection (over 20 years) for both marine and industrial service [6].

Several methods have been developed for the deposition of zinc coatings, one of which is zinc thermal spray metallizing using the TWEAS process. In this case, metallic zinc in the form of wire is fed to a torch, with which it is heated to its melting point. The resulting molten or nearly molten droplets are accelerated in a gas stream and projected against the surface to be coated (i.e., the substrate). On impact, the droplets flow into thin lamellar particles adhering to the surface, overlapping and interlocking as they solidify. The total coating thickness is usually generated in multiple passes of the coating device. Heat for melting is provided either by a combustion of an oxygen-fuel gas flame or an electric arc. In any case this method produces thick coatings composed of large sized grains. The intrinsic characteristics of these coatings are a high porosity and a very rough surface. Furthermore, due to the fast cooling procedure of the liquid droplets, diffusion at the Fe–Zn interface is inhibited and as a result, the coating adherence mechanism is mostly mechanical, depending on the kinetic energy of the sprayed particles, while no Fe–Zn alloy layers are present, as in the case of hot-dip galvanizing. A common phenomenon in the process industries is the oxidation of the exterior surface of steel pipes used in superheated steam or industries for anticorrosion applications. Thermally sprayed zinc, aluminum and zinc/aluminum alloy coatings that are produced by the TWEA spraying process find widespread applications in distribution and transmission pipes and electrical lines, bridges etc.

The aim of the present study is to compare the corrosion performance of Zn, Al and Zn/15Al coatings produced by the TWEA spraying process on steel surfaces in salt-spray environments.

2 EXPERIMENTAL

In this study, Zn-, Al- and Zn/15Al-coated mild-steel coupons were used. A Sulzer Metco Smartarc TWEA system and wires (pure zinc, pure Al and Zn/15Al, commercially) were used for the production of the coatings. The surface-coating types and the coating parameters of the coupons are given in **Table 1**. They are coated with the arc-spray deposition method by using different currents of (100, 200, and 300) A. These Zn-, Al- and Zn/15Al-coated steel coupons, which have nominal dimensions of (150 × 100 × 2) mm, were used for the structural examination and the corrosion testing.

After the surface coatings of the samples are completed, they are scribed with an Erichsen 463 scratch stylus. This hand-operated instrument complete with a carbide cutting tip provides a convenient means of scoring a 1-mm-wide rectangular track on the surface of the coating for the corrosion tests. A neutral (5 % NaCI) salt-spray corrosion that is frequently used in international applications, such as the automotive industry and military investigations, is applied to the prepared samples according to the ASTM B 117, D 1654 and D 1193 standards [7–14]. The surface is scribed up to the steel substrate according to ASTM D 1654 [16]. The samples were placed in an Angelantoni DCTC 600 P salt-spray test cabinet with an angle of 15–30° according to ASTM B 117 [15]. The structural analysis was carried out using a high-resolution camera in order to evaluate the surface characterization. A Deflesko positector 6000 FNS is used for measuring the thicknesses of the coatings. A cross-sectional examination using optical and scanning electron microscopy (SEM) was carried out after the surface polishing.

3 RESULTS AND DISCUSSION

3.1 Microstructural Investigation

The general structures of the Zn, Zn/15Al and Al coating are presented **Figure 1**. The Zn and Zn/15Al coating structures contain oxides, which are gray areas and less porosity in microstructure, but the coatings are relatively dense. There is little porosity but no oxide formation in the Al coating. The wavy surface of the Al coatings is due to the high melting temperature as well as the formation of a thin surface oxide film around the droplets. The EDS analyses results are shown in **Figure 2**. Although Zn and Zn/15Al have high oxygen peaks, the Al coating has a weak indication of an oxygen peak in the EDS analyses results. All the structures were revealed under the same coating conditions as shown in **Figure 1**.

The spray current value deals with the wire feed rate directly in the TWEAS process. When the arc current is

Table 1: Surface coating types and coating parameters of the steel coupons
Tabela 1: Vrste prekritij površine in parametri naprševanja vzprcev jekla

Number of sample	Zn Coating	Al Coating	Zn/15Al Coating	Wire Voltage /V	Current /A	Compressive Air bar	Spray Distance /mm
1	Applied	None	None	24	100	3	150
2	Applied	None	None	24	200	3	150
3	Applied	None	None	24	300	3	150
4	None	Applied	None	23	100	3	150
5	None	Applied	None	23	200	3	150
6	None	Applied	None	23	300	3	150
7	None	None	Applied	26	100	3	150
8	None	None	Applied	26	200	3	150
9	None	None	Applied	26	300	3	150

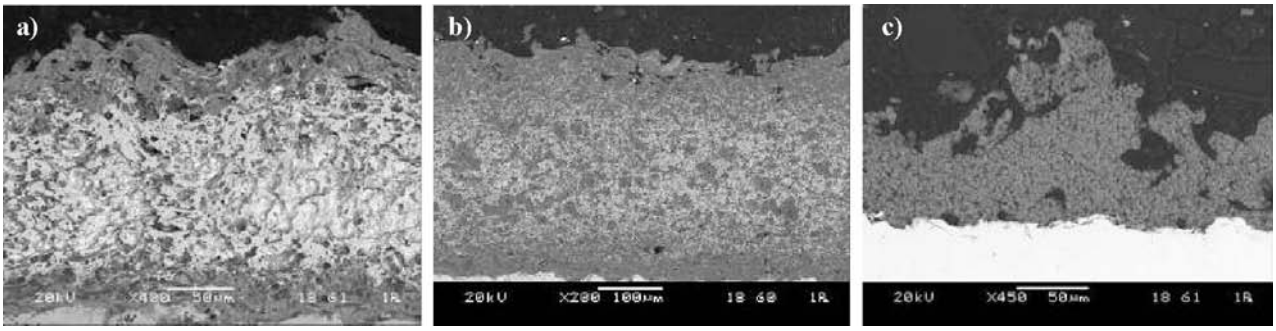

Figure 1: SEM microstructure of cross-section of coatings: a) Zn coating, b) Zn/15Al coating and c) Al coating
Slika 1: SEM mikrostrukture preseka prekritij: a) Zn plast, b) ZN/15 Al plast in c) Al plast

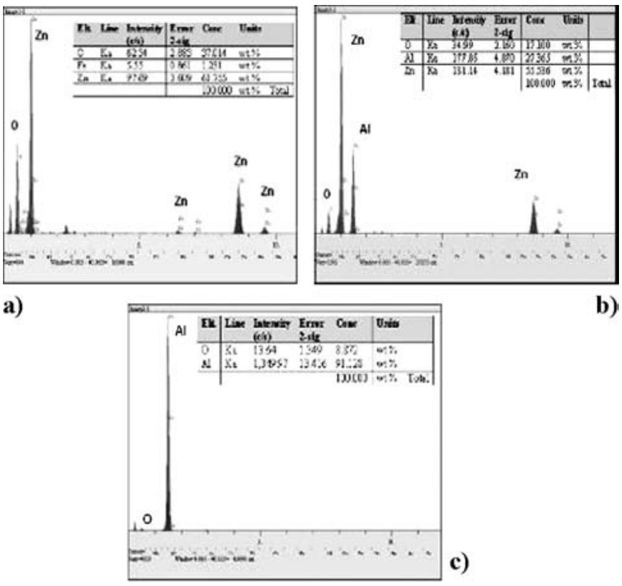

Figure 2: EDS analysis results of a) Zn coating, b) Zn/15Al coating and c) Al coating
Slika 2: EDS analiza a) Zn plasti, b) Zn/15Al plasti in c) Al plasti

increased, the wire feeding accelerates during the spray process. In this study, Zn, Al and Zn/15Al coatings were produced with different spray-current values of (100, 200, 300) A, a constant air pressure of 3 bar and 7 passes. The coating thickness changed with a different spray current. **Figure 3** shows that the coating thickness increases with a high spray current because of the low melting point of the Zn due to a high temperature with a high spray current because the high spray current composes the high wire feeding during the coating application. On the other hand, a high spray current of 300 A leads to overmelting of Zn, which spreads on the substrate surface. For Zn/15Al and Al the thickness of the coatings increased at a high spray current of 300 A due to high wire feeding onto the substrate, as can be seen in **Figure 4** and **Figure 5**.

When the coating process was carried out with a high arc current, the wire feed speed was increased. As a result the thickness of the coating increased. Furthermore, the Zn coating thickness was higher than for Zn/15Al because the melting point of the Zn is lower than for Zn/15Al. For comparison, it is clear that the thicknesses of Zn and Zn/15Al at a given current value are 200 µm and 170 µm, respectively. Nevertheless, all the coating thicknesses increased with high spray-current values. The variation of the coating thicknesses with the different spray currents and a constant air pressure (3 bar) is given in **Figure 6**.

3.2 Salt-spray corrosion test

The corrosion performance of Zn, Al, and Zn/15Al coatings produced with different currents of (100 A, 200 A, and 300) A are given in **Figure 7, Figure 8, and Figure 9**. It is clear that the corrosion performances of the Zn coatings produced with 100 A and 200 A were lower

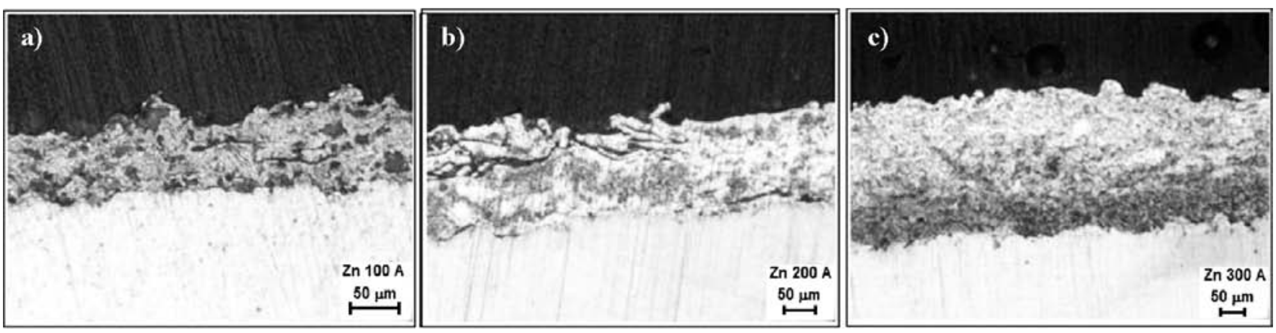

Figure 3: Zn coating with a different arc current; a) 100 A, b) 200 A, c) 300 A
Slika 3: Zn plast napršena z različnim tokom loka; a) 100 A, b) 200 A, c) 300 A

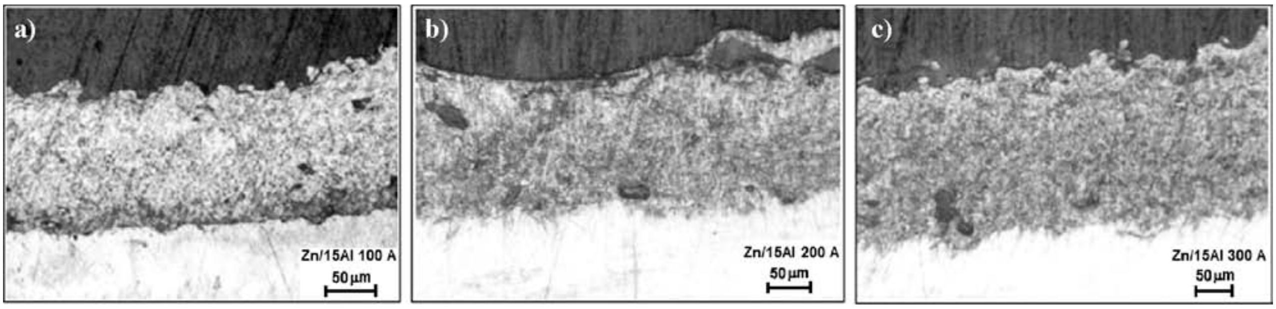

Figure 4: Zn/15Al coatings with different arc current; a) 100 A, b) 200 A, c) 300 A
Slika 4: Zn/15Al plast napršena z različnim tokom loka; a)100 A, b) 200 A, c) 300 A

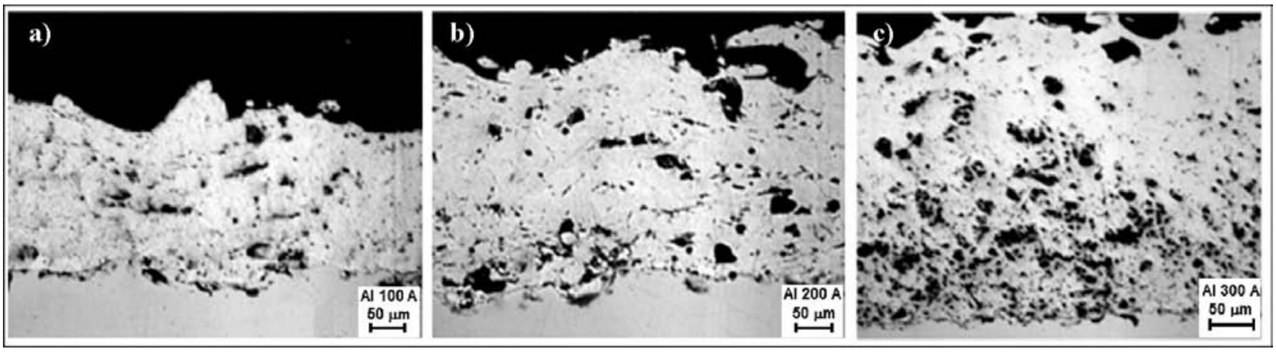

Figure 5: Al coatings with different arc current; a) 100 A, b) 200 A, c) 300 A
Slika 5: Al plast napršena z različnim tokom loka; a)100 A, b) 200 A, c) 300 A

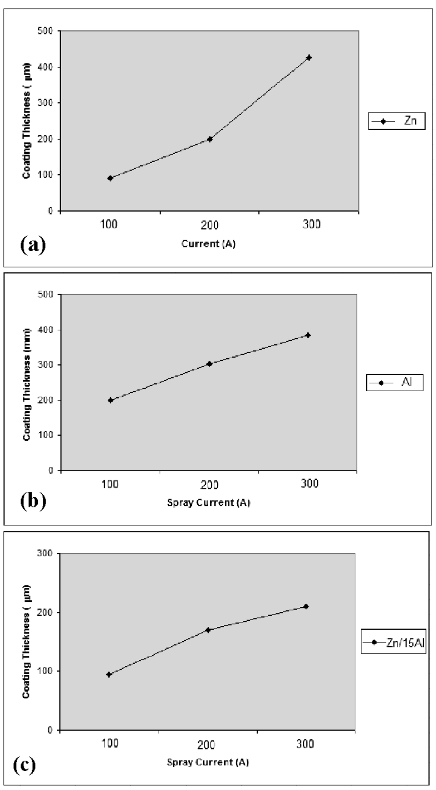

Figure 6: Influence of the arc current on the coating thickness at a constant pressure of 3 bar; a) Zn, b) Zn/Al 85/15, and c) Al (air pressure 3 bar)
Slika 6: Vpliv toka lokana debelino plasti pri konstantnem pritisku 3 bare; a) Zn, b) Zn/Al 85/15 in c) Al

than the Zn/15Al and Al coatings. Red rust initiation showed in these samples' coating surface, first after 500 hours. But no blistering, delamination and faults were found in the scribed area (R_s) for all of the samples. Zinc corrosion products (white rust) were found on the Zn and Zn/15Al coating surface and the white rust covered the scribed areas of this samples. There was no white rust on the Al-coated sample surfaces. No red rust was determined after 1000 h in the scribed area of the samples Zn and Al coatings produced with 300 A and all the

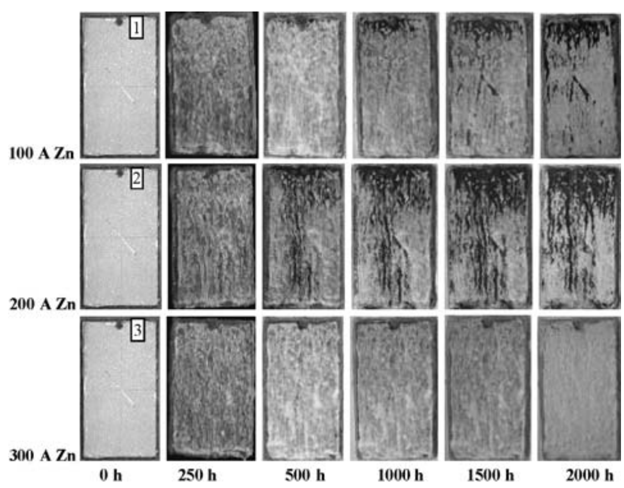

Figure 7: Images of the corrosion behaviors of Zn-coated samples during the salt-spray corrosion test
Slika 7: Posnetki korodiranih vzorcev z Zn plastjo med preizkusom slanega naprševanja

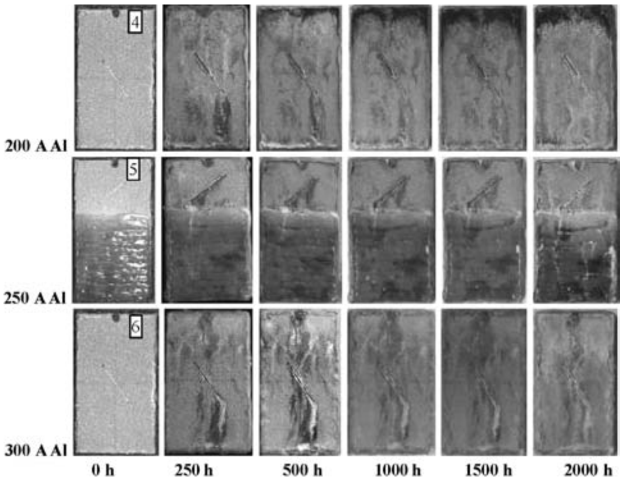

Figure 8: Images of the corrosion behaviors of Al-coated samples during the salt-spray corrosion test

Slika 8: Posnetki korodiranih vzorcev z Al Zn plastjo med preizkusom slanega nprševanja

Zn/15Al coatings. In the Al coatings, red rust occurred in the corners of the sample surfaces because of the lower coating thickness in the corners than in the middle of the coating surface. According to manual spraying application, a non-homogeneous coating thicknesses consists of Al coatings. In addition, the Al coating that was produced with 300 A has no red rust on the coating surface. Hamdy [18], has pointed out that no sign of corrosion was observed even after 2000 h of exposure in the salt-spray chamber on Al substrates. The Zn and Al coating produced with a high current value (300 A) showed the best corrosion resistance performance among the Zn- and Al-coated group, respectively. When the blistering and fallen coatings were evaluated for samples 2, the unscratched area (R_{us}) was found to be 0 and this result

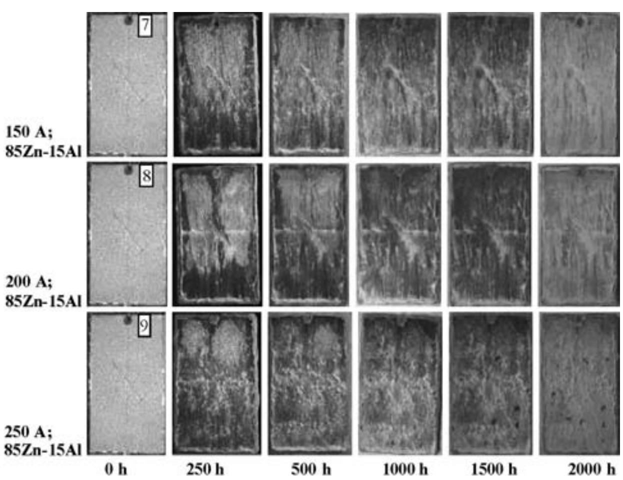

Figure 9: Images of the corrosion behaviors of Zn/15Al-coated samples during the salt-spray corrosion test

Slika 9: Posnetki korodiranih vzorcev z Zn/15Al plastjo med preizkusom slanega nprševanja

showed that the corrosion resistance of this sample is low according to ASTM D 1654 [16].

Zn and Al coatings produced at a high current showed a high corrosion-protection performance due to the increasing coating thickness during the salt-spray corrosion test period. It is revealed that the anti-corrosion performances of the Zn and Al coatings increased directly when the coating thickness of the Zn and Al coatings increased. In unscribed area R_{us} is determined as 0 as a result of taking the faulty regions (>75 %) on the surface of the sample into account in the evaluation. As a conclusion, Zn/15Al coatings showed a higher corrosion performance than other samples. In particular, all the Zn/15Al of the surfaces and the scribed area were covered with white rust.

As shown in **Figure 9**, the blistering is visible, after the corrosive solution reaches substrate 9 by going through the coating layer. Initially, as result of the corrosion on the surface of sample 9, the formation of the outer circle of the blister was observed. It was shown that the corrosion products blistered the coating layer by a volume expansion and peeled at the end of the corrosion test. It was observed that the Al (samples 4–6) and Zn/15Al (samples 7–9) coatings have a higher corrosion resistance than the Zn coating (samples 1–3) after 2000 h of salt-spray testing. The samples with numbers 8 gave the best result when it was evaluated for the scratched and the unscratched area. The salt-spray corrosion test results can explain that the Zn/15Al coating produced at 200 A showed a higher corrosion performance than the other coatings.

4 CONCLUSIONS

After the accelerated corrosion test (the salt-spray test), it is obvious that the corrosion resistances on the Al- and Zn/15Al-coated surfaces are better than the Zn-coated surfaces. As a result, it was found that the Al-coated surfaces were not affected very much by an aggressive chloride environment. For all of the Zn- and Zn/15Al-coated surfaces, the pitting and corrosion products (white rust) occurred during the salt-spray test. By comparing the different pre-treatments of the Al, Zn and Zn/15Al, it was found that the Zn/15Al coatings have a higher corrosion resistance than the Zn and Al coatings. According to the occurrence of the Zn corrosion products (white rust), the Zn- and Zn/15Al-coated steel substrates were protected against corrosion because of the sacrificial anode protection mechanisms of the Zn. Al creates a stable oxide on the coating surface and it protects from oxygen diffusion through the steel substrate as a known barrier effect. The Zn/15Al coating has two protection mechanisms together. The salt-spray measurements indicate that the Al and Zn/15Al systems are more suitable than the Zn system as far as protection against a chloride environment is concerned.

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