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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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 zinc 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 ¹.

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, me-
tallic 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 lamellae 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 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.

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Table 1: Surface coating types and coating parameters of the steel coupons

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Zn Coating</th>
<th>Al Coating</th>
<th>Zn/15Al Coating</th>
<th>Wire Voltage /V</th>
<th>Current /A</th>
<th>Compressive Air bar</th>
<th>Spray Distance /mm</th>
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<tr>
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<td>26</td>
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</tbody>
</table>
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...
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
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 thickness consists of Al coatings. In addition, the Al coating that was produced with 300 A has no red rust on the coating surface. Hamdy\textsuperscript{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 ($R_{u}$) was found to be 0 and this result showed that the corrosion resistance of this sample is low according to ASTM D 1654\textsuperscript{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 $R_{u}$, 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.
Acknowledgements

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