How to successfully battle corrosion: Thermally sprayed coatings of zinc and zinc alloys

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Abstract

Thermally sprayed coatings of zinc and zinc alloys currently form one of the predominant groups for corrosion protection of steel and concrete. Thermally sprayed coatings can alternatively be produced by techniques widely known as flame spraying and electrical arc spraying. The coating materials are available as wire.

Apart from spraying pure zinc, the most commercially sprayed zinc alloys are of the system zinc-aluminium. Some countries of the world take advantage of metallising steel constructions utilising electrical arc spraying. Surface protection is realised by forming a coating of zinc or zinc alloys in combination with a paint. The coating is able to form protective layers and can also work as sacrificial anode. Properly sealed and painted such a coating can successfully serve for more than 20 years.

Materials development requires a wide range of test methods. This paper discusses properties of different zinc and zinc based alloys. Microstructure and the corrosion resistance of unpainted arc sprayed coatings are revealed. In conclusion these properties lead to coating applications in various corrosion situations to successfully battle corrosion.

1 Introduction

Zinc or zinc alloy coatings have most widely been used for corrosion protection of steel for years [1]. Several methods of coating techniques are known: hot dipping, electroplating, thermal spraying or painting. Each technique affects obtainable coating properties as adhesion between coating and substrate material, coating thickness and uniformity, mechanical properties or formability of the system coating-substrate. Coating requirements and the nature and geometry of the workpiece which is to be protected decisively dictate the selection of the appropriate coating technology. If good mechanical interlocking, considerable mechanical strength and a coating thickness in a range from 10μm to several mm are required, thermal spraying is able to deliver. Figure 1 illustrates the arc spray process to coat steel tubes with a corrosion protective material.

2 Zinc and Zinc Alloys

2.1 Zinc

Corrosion protection of steel through pure zinc coatings has been well known for decades. The principle of corrosion protection through zinc is a chemical reaction on top of the zinc coating at the interface zinc/surrounding atmosphere. Pure zinc coatings initially form zinc oxide in case oxygen is offered by the environment.

The availability of atmospheric carbon dioxide, salt and other impurities is crucial for the chemical reaction leading to zinc hydroxide and zinc carbonate.
The formation of protective layers is controlled by the pH of the surrounding atmosphere. Zinc coatings obtain their highest corrosion protection in pH-regions between 6 and 12.5. Figure 2 illustrates the variation of the corrosion rate with the pH.

2.1 Zinc-Aluminium

The same amphoteric behaviour as for zinc can be observed for aluminium. The interface reaction aluminium/atmosphere leads to the formation of highly stable oxide layers.

As discussed zinc is relatively stable in the basic region. In contrast aluminium is very well known for its stability in the neutral and acid region as figure 3 demonstrates.

Alloying of pure zinc with aluminium has gained interest in thermal spraying. ZnAl-alloys offer advantages in corrosion resistance as they cover a area vast area of corrosion resistance. Thus a comprehensive protection can be obtained (figure 4).

Applying ZnAl-coatings on steel affect passive protection by the coating surface and active protection through cathodic protection for steel. Thus two important factors for corrosion protection are combined.

The zinc aluminium-system, illustrated in figure 5, indicates conditions preferred for useful alloys at both ends of the system [5]. The solubility of sold zinc in aluminium is extensive whereas the solubility of solid aluminium in zinc is limited. The eutectic value is at 5% Al-content (381°C), the eutectoid composition is at 78% Zn (277°C).

Today the most important alloy for thermal spraying is made of ZnAl 15. Also available but of less meaning are wires made of hypereutectic ZnAl 2, eutectic ZnAl 5. Additionally - for this study only - wire made of eutectoid ZnAl 22 was manufactured at the GRILLO R&D-labs in Duisburg, Germany. So-called pseudo alloys processed by feeding two different wires (Zn, Al) to the gun were of interest, too.

3 Thermal Spraying

Thermal spray processes are characterised by liquid droplets depositing onto a surface. The coating material is injected into the heat source in which it melts. An atomiser gas accelerates the molten particles towards the substrate material. On impact at the substrate surface the droplets solidify and adhere both to the substrate and to each other forming a coating.

Thermally sprayed coatings may have a thickness ranging from 50μm up to a few mm depending on the material being deposited. The thermal spray process combines thermal energy for melting or heating particles for surface coating with kinetic energy for particles forming the surface layer. The thermal energy may be provided by fuel and oxygen, electrical heating or radiation. Kinetic energy is usually provided by a gas jet.

Coating materials are generally solid and are fed to the energy source as powder, rod or wire [6]. The family of thermal spray technologies consists of plasma spraying,
electrical arc spraying, laser spraying and flame spraying including high velocity oxygen fuel spraying.

Thermally sprayed coatings of zinc or zinc alloys can alternatively be produced by techniques widely known as flame (acetylene-oxygen or propane-oxygen) spraying and electrical arc spraying.

Today arc spraying has gained greater attention as it offers advantages in efficiency and lower costs. In general equipment for arc spraying is more expensive than it is for flame spraying. However higher investment costs can rapidly be assimilated by the higher efficiency and lower operating cost of the arc spray system, as table 1 indicates.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Flame spraying</th>
<th>Arc spraying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquefaction of zinc, kg/h</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>Energy costs for liquefying zinc, $/h</td>
<td>≈28</td>
<td>≈25</td>
</tr>
<tr>
<td>Effective use, min/h</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Effective use, kg/h</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Energy costs, $/m² ($/kg equals $/m² at 100 μm zinc thickness)</td>
<td>2.33</td>
<td>0.11</td>
</tr>
<tr>
<td>Spraying speed, m³/h for 100 μm zinc</td>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>Wage costs, $/m² at 60 $/h</td>
<td>4.17</td>
<td>2.17</td>
</tr>
<tr>
<td>Total costs, $/m²</td>
<td>6.50</td>
<td>2.26</td>
</tr>
</tbody>
</table>

### 3.1 Flame Spraying

Flame spraying (figure 6) utilises the chemical energy of oxidising fuel gases (e.g. acetylene) in combination with oxygen to obtain a high combustion temperature resulting in the formation of a high temperature jet. Wires are introduced into the jet, melted and accelerated to the substrate surface by the expanding gas flow. Jet gas speeds are typically below 100 m/s generating particle speeds up to 80 m/s. The flame jet temperature is generally above 2,500°C. The flame spraying process allows a lamella coatings of 85-90 % density.

![Figure 6. Flame Spraying](image)

### 3.2 Arc spraying

Arc spraying (figure 7) involves the generation of an electrical arc between the ends of two wires to be melted. The molten material is atomised utilising high velocity compressed air stream to accelerate the particles towards the surface to be coated.

![Figure 7. Principle of arc spraying](image)

The whole spraying system includes a the spray gun, a feeding system and power source. A complete system for corrosion protection is shown in figure 8.

![Figure 8. Arc spray system for corrosion protection (OSU-Maschinenbau, Germany)](image)

### 4 Arc Spraying of Zinc and Zinc-Alloys

#### 4.1 Process Parameters

For this study wires made of Zn, ZnAl 2, ZnAl 5, ZnAl 15, ZnAl 22 and Al were available and arc sprayed...
Coatings were manufactured. Additionally two different pseudo alloys were produced. Therefore two wires made of different material, but same diameter, were fed into the gun (Zn-Al, ZnAl 15 - Al). Table two summarises the properties of the wires used.

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition[wt.-%]</th>
<th>Density [g/cm³]</th>
<th>Melting Point [℃]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>99.99</td>
<td>-</td>
<td>419</td>
</tr>
<tr>
<td>ZnAl 12</td>
<td>97.5-98.5</td>
<td>1.5-2.5</td>
<td>6.89-7.01</td>
</tr>
<tr>
<td>ZnAl 15</td>
<td>94.5-95.5</td>
<td>4.5-5.5</td>
<td>6.57-6.68</td>
</tr>
<tr>
<td>ZnAl 15</td>
<td>84.5-85.5</td>
<td>14.5-15.5</td>
<td>5.71-5.78</td>
</tr>
<tr>
<td>ZnAl 22</td>
<td>77.5-79</td>
<td>21-22.5</td>
<td>5.22-5.32</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>99.5</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Coatings were processed at the Grillo R&D labs employing an OSU-arc spraying system.

Selecting appropriate spraying parameters is crucial for the coating structure and performance. Therefore the thermal properties (table 3) of the materials to be sprayed have to be considered.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Point T_mel [℃]</th>
<th>Boiling Point T_boil [℃]</th>
<th>Thermal Conductivity λ [W/mK]</th>
<th>Thermal Capacity c_p [kJ/kgK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>419</td>
<td>906</td>
<td>113</td>
<td>0.39</td>
</tr>
<tr>
<td>Al</td>
<td>660</td>
<td>2450</td>
<td>239</td>
<td>0.88</td>
</tr>
</tbody>
</table>

The addition of aluminium to zinc requires an increased energy input to melt the alloy homogenously. However, one has to take into account that too much energy input may cause the loss of zinc during spraying as its boiling temperature is relatively low.

These considerations led to the development of parameter sets shown in table 4.

<table>
<thead>
<tr>
<th>Wire</th>
<th>Wire Diameter [mm]</th>
<th>Voltage [V]</th>
<th>Current [A]</th>
<th>Spraying Distance [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>99.9</td>
<td>2.5 mm</td>
<td>20</td>
<td>&gt;250</td>
</tr>
<tr>
<td>ZnAl 12</td>
<td>2 mm</td>
<td>22</td>
<td>&gt;250</td>
<td>160-180</td>
</tr>
<tr>
<td>ZnAl 15</td>
<td>2 mm</td>
<td>22</td>
<td>&gt;250</td>
<td>160-180</td>
</tr>
<tr>
<td>ZnAl 15</td>
<td>2.5 mm</td>
<td>23</td>
<td>&gt;250</td>
<td>160-180</td>
</tr>
<tr>
<td>ZnAl 22</td>
<td>3.17 mm</td>
<td>24</td>
<td>&gt;250</td>
<td>160-180</td>
</tr>
<tr>
<td>Zn-Al pseudo</td>
<td>2.5mm/2.5mm</td>
<td>24</td>
<td>&gt;250</td>
<td>160-180</td>
</tr>
<tr>
<td>Al</td>
<td>2.5</td>
<td>29</td>
<td>&gt;250</td>
<td>180</td>
</tr>
</tbody>
</table>

Steel samples were coated in a thickness of 150µm. After spraying the samples were characterised to reveal the individual coating performance.

A wide range of test methods was available and coating characteristics as the microstructure (metallographic investigations, porosity control, surface morphology),

mechanical properties (adhesion strength, hardness) corrosion resistance (alternating dipping tests in NaCl, salt spraying tests, corrosion in different atmospheres) have to be evaluated carefully.

Simulation of different atmospheres and electrochemical or mechanical loading situations enable manufactures and customers to select a coating systems suiting their needs.

### 4.2 Morphology and Microstructure

The evaluation of coating’s morphology includes coating thickness and porosity, crack formation and surface topography (i.e. surface roughness). Techniques such as light microscopy, scanning electron microscopy, image analysis and surface analysis are employed usually. Processing parameters allow the control of many morphologic features.

Micrograph preparation and microscopic examination allows to compare the coating’s microstructure. Different coating morphologies of arc sprayed zinc (figure 9), arc sprayed ZnAl 15 (figure 10) and arc sprayed pseudo alloy Zn/Al (figure 11) can be observed.

![Figure 9. Zinc Coating (arc sprayed)](image)

![Figure 10. ZnAl 15 coating (arc sprayed)](image)

![Figure 11. ZnAl pseudo alloys](image)
For all types of coatings no metallurgical interaction between substrate and coating can be observed. The grit-blasted and roughened substrate surface allows a sufficient mechanical bond within the interface substrate/coating.

Pure zinc coatings typically are characterised by a very homogeneous structure showing the lamellar structure which is to be expected for arc sprayed coatings\[6\]. Pre-alloyed wires also produce coatings characterised by a homogeneous structure. By contrast pseudo alloy coatings obviously consist of different phases (dark and light areas in fig. 11). Zhongli et al. \[9\] identified three different phases in ZnAl-pseudo alloys: a pure zinc phase, a pure aluminium phase and a zinc-aluminium phase. As matter of fact the presence of three different phases leads to structural inhomogenities in ZnAl-pseudo alloy coatings.

Micrographs can also be employed to determine the porosity of the coatings. The porosity percentage can be calculated by analysing systems taking advantage of digitalised photographs.

Figure 12 illustrates the calculated porosities of the evaluated coating systems. The porosity of all materials was measured in a region between 9.5 and 11.8%. These values can be expected for arc sprayed metal coatings\[6\].

According to DIN EN 24 624 and EN 582 a minimum adhesive strength of 6 MPa is required for zinc and zinc-aluminium and aluminium coatings of 200\textmu m\[10\].

Applying a sealer on top of the metal coatings may enhance the adhesion strength in the interface substrate/coating\[11\].

4.3.2 Tensile Strength

A test to determine the tensile strength of the coating was designed. Therefore thick coatings were sprayed on a smooth glass surface. These coatings could be detached easily.

Samples for tensile strength measurements were prepared from the detached coatings. These samples were evaluated with regards to their tensile strength. The tensile strength values were calculated. The results are shown in figure 13.

The homogenous nature of the coatings made of pure zinc and zinc-aluminium wires leads to higher tensile strength values compared to coatings made of pseudo alloys and pure aluminium. The decreased tensile strength for pseudo alloys could be expected after revealing the multi-phase structure of the coating earlier. Aluminium coatings seem to be weaker as the tendency to form oxides during spraying is higher while spraying in air. Oxide particles may be responsible for a decreased tensile strength.

4.4 Corrosion tests

Corrosion tests are generally applied to coatings created to increase surface corrosion resistance. In case of this study two different tests were conducted:

1. test according to German standard DIN 50021-SS (salts pray test)

2. test according to german standard DIN 50018-KFW 0.2S (condensation water test)
Both tests are tools to evaluate the corrosion behaviour of the coatings. Thickness and weight of each sample have to be determined before and after the corrosion test. Additionally the structure of the surface can be judged by follow-ups applying different visual techniques as light microscopy.

Weight was determined using a high sensitive balance. Thickness measurement were performed by a gauge based on the magnetic inductive principle.

Before determining changes in weight and structure of the surface the corrosion products were removed by etching.

### 4.4.1 Salt spray test

Samples were tested in an atmosphere consisting of salt spray mist containing sodium chloride keeping the temperature at 35°C ± 2°C.

The thickness reduction for the coatings was evaluated after being exposed to the salt mist for 168 h. The results are as illustrated in figure 14.

![Figure 14. Thickness reduction vs. Aluminium content after 168 h salt spray test](image1)

Mass reduction results suggest that the addition of aluminium to zinc improves the corrosion resistance dramatically under salt spray conditions.

Obviously there is a maximum for the corrosion protection within the system Zn-Al at 15 wt.-% aluminium. Compare to pure zinc the corrosion resistance is 10 times higher in the salt mist atmosphere. Pseudo alloy coatings also show an improved corrosion resistance compare to pure zinc coatings. However, the multi-phase structure prevents pseudo alloys from achieving results as positive pre-alloyed coatings.

However, increasing the aluminium content jeopardises the coatings functionality by an increased number of pittings. ZnAl pseudo alloys show a slightly increased mass reduction compare to ZnAl 15 wires.

Figure 15 shows the surface of a zinc coating after 1320 h salt spray test illustrating the corrosion products on top of the zinc coating.

![Figure 15. Surface of arc sprayed Zn-coating after 1320h salt spray test](image2)

The beginning of red rust was recorded as well (figure 16). First signs of red rust can be detected after 300-500 hours exposure to salt mist for pure zinc coatings. For zinc-aluminium alloys the formation of red rust starts delayed after 500-900 h exposure. In contrast the red rust formation on aluminium coated samples started between 0 and 50 hours exposure.

![Figure 16. Red rust formation in salt spray test](image3)

### 4.4.2 SO2-test

This test is based on alternating the atmosphere in a closed chamber between condensing water and sulphur dioxide. The sulphur dioxide atmosphere is realised by a SO2-concentration of 0.067 Vol.-% at 100% humidity and 40°C temperature. Normal atmospheric conditions are defined at a humidity level less than 100% and at a temperature of 23°C.

One test cycle is defined as 16 h normal atmosphere followed by 8 h SO2-atmosphere.

Figure 17 illustrates the results for coatings made of wires containing different amounts of aluminium. Coatings
made of ZnAl 15 wire show the most favourable behaviour, no mass reduction could be observed after 30 test cycles. Pure zinc coatings are clearly non resistant against SO$_2$-atmosphere, the ZnAl pseudo alloy has an improved corrosion resistance based on the zinc result, but it is not as outstanding as the ZnAl 15 result.

The results of various studies resulted in developing various standards suggesting how to apply zinc and zinc aluminium coatings as shown in table 5.

### Table 5.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Metal</th>
<th>Zinc</th>
<th>Zinc-Aluminium 85-15</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unpainted</td>
<td>Painted</td>
<td>Unpainted</td>
</tr>
<tr>
<td>Salt water</td>
<td>N.R.</td>
<td>100</td>
<td>N.R.</td>
</tr>
<tr>
<td>Fresh water</td>
<td>200</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>Urban environment</td>
<td>100</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Industrial environment</td>
<td>N.R.</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>marine atmosphere</td>
<td>150</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>dry indoor environment</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>N.R.: Not recommended</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Practice and experience have shown that these very general values have to be modified depending on the specific application, atmosphere, temperature etc..

Today thermally sprayed coatings are applied for long-term corrosion protection for steel structures and steel-reinforced concrete structures. Working principles are active galvanic protection or cathodic protection. The product range is wide: from small workpieces to large steel reinforced concrete buildings everything can be coated. Coating systems are available as stationary system, but also as mobile units employable on building sides.

Figure 19 illustrates the application of zinc for active galvanic protection for a small garden gate made of steel.

In contrast figure 20 shows the application of arc sprayed zinc coatings for the cathodic protection of the Tsing-Ma bridge in Hong Kong.

### 5 Applications

Coatings of zinc aluminium can be sealed in the same way as zinc coatings are. The application of a coating of 100-400μm thickness allows to increase the lifetime of the corrosion protection system dramatically. Commercially available sealers are based on either poly vinyl chloride, acrylate, epoxy resin or polyurethane. The combination of zinc coating and paint allows to design coatings of highest corrosion resistance.
6 Discussion

The results of this work show that the thermally sprayed coatings of GRILLO-zinc aluminium wires produce coatings of a structure and morphology comparable to pure zinc coatings.

Thermal spraying of zinc-aluminium wires requires the modified process parameters to obtain coatings of a outstanding quality. In order to optimise the spraying parameters the different material properties of aluminium have to be taken into account.

The mechanical strength of pre-alloyed zinc aluminium coatings is sufficiently high enough to resist typical mechanical load situations while being applied as corrosion protective coating.

The result strongly suggest that the addition of aluminium to the zinc improves the corrosion resistance in marine and industrial environment. Best results were obtained in the region of the 15%-aluminium addition. In both tests, salt spray and SO$_2$ the corrosion resistance dramatically increased compared to zinc coatings, which is in accordance to Schulz et al. [12]. In conclusion there are new and extended applications for zinc based thermally sprayed coatings to provide long-term corrosion protection at lower pH levels even without paint.

However, the mechanical strength of pseudo alloy zinc aluminium coatings decreases as their multi-phase microstructure is too inhomogenous.

7 Summary

A test set up was designed in order to evaluate the mechanical and chemical performance of zinc and zinc aluminium coating. Whereas the mechanical performance of both systems is similar, differences in corrosion protection became obvious. The protective effect of arc sprayed zinc is sufficient in an atmosphere where the pH is in a range from 7 to 12. For lower pH zinc aluminium, alloys containing 15 wt.-% aluminium offer corrosion protection to pH values as low as 4.5 (table 6).

Table 6: GRILLO wires for corrosion protection

<table>
<thead>
<tr>
<th></th>
<th>GRILLO Zn 99.9 (flame and arc spraying)</th>
<th>GRILLO ZnAl 15 (arc spraying)</th>
<th>GRILLO ZnAl 15 (flame spraying)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH range</td>
<td>7-12</td>
<td>4.5-12</td>
<td>4.5-12</td>
</tr>
<tr>
<td>atmospheric corrosion resistance</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>SO$_2$ corrosion resistance</td>
<td>.</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

Thus, applying commercially available GRILLO-zinc and GRILLO-zinc-aluminium enables the customer to cover a wide range of corrosion protection applications. Additionally tailor made zinc based alloys for special applications are developed by GRILLO to meet the customers goals.

8 References


8. DVS-Merkblatt 2301 Thermische Spritzverfahren für metallischen und nichtmetallische Werkstoffe, DVS.-Verlag Düsseldorf 1987


10. DVS-Merkblatt 2302 Korrosionsschutz von Stählen durch thermisch gespritzte Überzüge, DVS-Verlag, Düsseldorf 1995

11. Schulz, W.D., Seidel, M., Spriestersbach, J. Influence of post coatings on the adhesion strength of metal spray layers out of zinc and aluminium, in DVS Berichte 175,