Effects of the sealing process on the corrosion behaviour of thermally sprayed and sealed coatings for corrosion protection of large building parts

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Summary

For use as corrosion protection in particularly critical environments thermally sprayed coatings based on Zn, Al and their alloys in combination with one or multiple organic intermediary and cover coats supply many advantages.

The subject of the research project described herein is the development of more in-depth knowledge of the influence of sealing process parameters on the corrosion behaviour of the coating system. This objective is reached through an evaluation of common coating characteristics, like the coat thickness, porosity, coat roughness, and adhesive strength. Specifically examined process parameters and determining factors are found in the thermal spraying process itself, the injection parameters and in particular, the sealing process.

In order to determine the weak points of the coatings as dependent on the production processes and production parameters, the samples were additionally tested for their corrosion resistance (e.g. lab tests in an artificial atmosphere, electrochemical measuring procedures). An assessment of the coating quality (e.g. thickness, coating defects, presence of residues or pores etc.) after the corrosion tests were carried out.

With regard to the sealing process, a significant improvement of the described coating characteristics thus far has been proven in the sealing. Moreover, the surface is evened out. Greater adhesive strength of the coating is evident in the same way as improved corrosion resistance of the coating system. Furthermore, corresponding characteristics were found in the different viscosity settings of the sealing medium. Especially too strong a dilution proves not to be expedient for the corrosion protection effect.

The overarching aim of the research work is to develop recommendations at the end of the project for the standardisation process based on the insights gained, so that these can be implemented in practice by the user in the near term.

1 Introduction

Steel is used as a building material because of its characteristics and the possibilities for efficient use. In reinforced condition, it corrodes in urban as well as in maritime or industrial environments. This corrosion on steel structures leads to immense ecological damages and economic losses globally each year. The present and future aim is to create a sustainable and durable corrosion protection through coating systems.

In order to protect iron and steel based structures against corrosion, protective coatings respectively coating systems are usually deposited.
For the hard working environments such as industrial and maritime weather conditions there is a multitude of options in the market to design coating systems [1, 2, 3]. Coating systems based on thermally sprayed layers have always lent themselves specifically for protection of large-dimensioned buildings (e.g. in the wind energy sector primarily in coastal and offshore regions, bridge engineering, etc.). Primarily Zn, Al and their alloys are processed in thermal spraying methods. These coatings are used as primer-coats in duplex coating systems [2, 3, 4].

Thermally sprayed zinc/aluminium-based coatings in combination with sealing and other organic layers (so-called “duplex systems”) offer a long-term corrosion protection for periods of more than 20 years [1, 2, 3, 5, 6] in particularly critical environments.

These materials are applied on the steel surface material in wire form by thermal spraying methods such as arc spray and wire-flame spraying [7]. The created layers usually have a certain measure of porosity (normally up to 15%) and oxides. It is necessary to close the porosity of the layers (the pores which are open on the surface) respectively to reduce the inner porosity of the layers using suitable sealing methods in order to achieve suitable corrosion protection. In the construction sector organic coating materials are used. These materials require good wetting and penetration behaviour [7] in order to fill the micro-porosity of the thermally sprayed coatings with the sealing.

The sealed thermally sprayed coatings provide a stronger barrier effect as an unsealed, as the thermal sprayed layer porosity inherent in the method is reduced or closed as a result of the sealing [2, 3].

From a scientific point of view, there is currently not enough information with regards to the behaviour of sealing materials in reference to the quality of thermally sprayed layers on zinc and aluminium basis, their penetration behaviour in thermally sprayed layers and the procedure of sealing processes. Scientific studies were carried out to answer these questions. A part of these results are introduced here.

2 Experimental

2.1 Coating materials and manufacturing of the coatings

As part of the studies discussed in this context, the Zn85Al15 alloy in the wire thickness of 2.5 mm was used as a spraying material for the manufacture of thermally sprayed coatings [according to 8]. An organic coating material containing 2K-micaceous iron ore on epoxy resin basis was chosen as seal. The thinner share was varied during the processing of this coating material (with 5%; 15% and 40% thinner).

2.1.1 Surface preparation of the base material

The substrates used corresponded to steel grade S235JRG2. After labeling and evaluation of the degree of rust of the samples the surface preparation was carried out. In order to achieve an adequate adhesive strength of the coatings the surface of the substrates was pre-treated by blasting. This took place prior thermal spraying. As abrasive grit for the blast-cleaning process corundum (F-016 grain) was used. The objective of the surface preparation was to roughen up the surface and remove impurities up to a surface preparation grade of at least Sa2½G or better (according to 9, 10, 11). Finally, the surfaces to be coated underwent cleanliness and roughness checks (using the profile comparators and also the contact profile method).
2.1.2 Thermal Spraying

The thermal spraying started immediately after completion of the surface preparation (blasting, surface check) in order to prevent contamination of the prepared surface or limitation of the adhesive due to humidity absorption and/or starting oxide formation. The coatings were applied in consideration of the spray positions (i.e. Horizontal, Flat and Overhead) by Arc Spraying (OSU Arc Spraying Plant). The spray parameters: Current values, voltage values, wire speed, atomizer pressure etc. were kept identical for all samples. Increased overspray was to be expected in the Flat position which would show on the samples. The samples surfaces were cleaned with dry, unoiled pressurized air immediately before/during and after applying the spray jet in order to minimize these adhesion reducing coatings.

A 100 µm coating thickness was selected as target thickness. An assessment of the atmospheric conditions (humidity, dew point, ambient air and sample temperature) was carried out and recorded before thermal spray application begins. Table 1 depicts the spraying parameters used in the investigation for thermally spraying.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spraying parameters</th>
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<tbody>
<tr>
<td></td>
<td>Spraying Position</td>
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<tr>
<td>Samples System 1 (P1…)</td>
<td>Horizontal</td>
</tr>
<tr>
<td>Samples System 2 (P2…)</td>
<td>Flat</td>
</tr>
<tr>
<td>Samples System 3 (P3…)</td>
<td>Overhead</td>
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2.1.3 The sealing post-treatment of the thermal sprayed coatings

A part of the thermally sprayed samples was sealed. The aim of the seal is to reduce the inner porosity of the sprayed layers by applying a coating. A thorough cleaning of the sprayed surface with the removal of spray dust and spray particles was envisaged before the sealing process and undertaken by blowing using compressed dry air. The organic coating material was processed according to the specifications of the coating material manufacturer. The seal was applied using airless spray processes with the spray plant "WIWA PROFESSIONAL 28064 Airless". Table 2 includes the product data of the coating material.

<table>
<thead>
<tr>
<th>Product data organic coating material</th>
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<tbody>
<tr>
<td>Coating material</td>
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<tr>
<td>Coating containing 2K-micaceous iron ore on</td>
</tr>
<tr>
<td>epoxy resin basis</td>
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<tr>
<td>Color</td>
</tr>
<tr>
<td>grey, DB 702</td>
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<tr>
<td>Density liquid</td>
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<td>approx. 1,6 kg/l</td>
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The influence of the spray position was studied by coating the panels in the same way as for thermal spraying in the three spray positions: Horizontal (Q), Flat (W) and Overhead (U). For this purpose, a reproducible, even application of the coating material was adhered to.
A further parameter for the sealing of the samples has been to vary the share of thinner. Three variations of test bodies were created. The first variation used 5%-share of thinner. The 2nd category of samples used the organic coating material in addition to thinner to thin it down to a 15% share and the thermally sprayed substrates were coated in the 3 above mentioned spray positions. After further applications of thinner up to a share of 40%, the third part of the thermally sprayed layers was coated under the same conditions.

The panels were coated individually. The panels were stored for approx. 18 hours in an air-conditioned drying chamber at 22 °C air temperature and 39.7% humidity. A total of 72 samples were created by thermal spraying and coating. The study results of 12 samples are presented in this context. Table 3 shows a summary of the characteristics of the studied samples.

Table 3: Summary of the samples characteristics

<table>
<thead>
<tr>
<th>Manufacturing characteristics</th>
<th>Sample (P)</th>
<th>1</th>
<th>1.1</th>
<th>1.2</th>
<th>1.3</th>
<th>2</th>
<th>2.1</th>
<th>2.2</th>
<th>3</th>
<th>3.1</th>
<th>3.2</th>
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<tbody>
<tr>
<td>TS</td>
<td>X</td>
<td>X</td>
<td></td>
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<td></td>
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<tr>
<td>TS + S with 5 %- thinner</td>
<td>X</td>
<td>X</td>
<td></td>
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<tr>
<td>TS + S with 15 %- thinner</td>
<td>X</td>
<td>X</td>
<td></td>
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<td></td>
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<tr>
<td>TS + S with 40 %- thinner</td>
<td>X</td>
<td>X</td>
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<tr>
<td>TS = thermally sprayed coating (target value 100 µm); S = Sealer ([NDFT] &lt; 40 µm)</td>
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2.2 Experimental concept and procedure

2.2.1 Coatings characterization

The coatings were examined with/without metallography preparations. The study methods were selected according to [9, 10, 11] as well as according to tests carried out for industrial manufacture.

The manufactured layers were examined in the state of "as sprayed" and "as sprayed and sealed" and the coating quality was evaluated with regards to visual appearance, roughness, adhesive strength etc.

The coating thicknesses were measured using a magnetic-inductive procedure. The contact profile method was used for the roughness measurements. For the pull off tests (adhesive bond strength), the samples were cut out on the outer circumference of the dollies.

The layer quality was also evaluated with microscopic methods (light microscope, scanning electron microscope) (e.g. coatings thickness measurement, coatings quality, presence of blasting material residue and/or pores, coating material failure, topography of the surface, penetration of seal etc.). Metallographical cross sections were prepared with epoxy resin. First the samples were impregnated with a fluorescent dye in order to make the existing pores more visible. The results were documented using microscopic images.

2.2.2 Study of the corrosion behaviour of the coatings

The corrosion tests (salt spray test (NSS) according to EN ISO 9227) were carried out to study the behaviour of the coatings with regards to corrosion resistance and to determine the "weak points" of the layers in dependence of the manufacturing processes and the manufacturing parameters.
The samples were weighed before and after the exposure. Images of the samples were taken with a Bookeye scanner after the completion of the salt spray test. The image was analysed with the ImageJ program. This allowed the calculation of the slightly corroded/heavily corroded and not corroded areas. The layer quality was checked again after the completion of the tests.

3 Results and Discussions

3.1 Characterization of coatings

3.2.1 Characterization of coatings without metallography preparation

The roughness of the substrate after surface preparation by blasting was determined. The average mean roughness value was $R_z = 63.9 \, \mu m$ for all substrates. The minimum roughness value was identified for the sample substrates P1.3 and P2.2. (approx. 55-60 $\mu m$). The higher values were measured for the substrates P2 and P1.1. (approx. 75-80 $\mu m$).

After thermal spraying, all samples showed no irregularities in the coating surface quality (visual check). Only the surface structure of the layer could be recognized, in parts based on the completed paths (for thermal spraying process). Throughout, the coverage was great and no inclusions could be recognized.

After sealing, no irregularities in the shape of layer discontinuity, cracks or visible pores, inclusions of foreign particles in the layer surface quality could be identified. At times, small bubbles showed in the seal (in dry state).

By compare the roughness of thermally sprayed coatings with each other, then can be noted that the roughness values of coatings sprayed in Horizontal - spray position ($R_z$-values of approx. 95 $\mu m$) are above the level of the Flat and overhead position ($R_z$-values of approx. 85 $\mu m$).

Noticeable for the evaluation of the surface roughness after sealing was that the roughness value ($R_z$) of the sealed samples P1.3, P2.3 and P3.3 (Sealer with 40 %-thinner) were comparable with the Rz-values of thermally sprayed coatings. Other sealed samples showed a trend of a reduction in surface roughness values between the thermal spraying and the sealing process (Figure 1).

![Figure 1](image_url)
It was ascertained for the magnetic-inductive measuring of thickness of the thermally sprayed coatings that all layers achieved the target value of 100 µm. It was noted by evaluating the results in consideration of the spray position characteristics that the Horizontal- and Flat- position sprayed coatings showed greater layer thickness values as those sprayed form the Overhead position.

By compare the thermally sprayed sealed layers to each other, then it can be noted that the thickness of the sealed samples P1.3, P2.3 and P3.3 (sealer with 40%-thinner) are below the level of the sealing variations 1 and or close to the thickness values of the thermally sprayed coatings (Figure 2a).

An increase of the total coating thickness (TS+S) was observed by reducing of the degree of dilution of the seal.

Significant differences between the adhesive bond strength values of the thermally sprayed or thermally sprayed and sealed samples could not be determined (Figure 2b).

![Figure 2: Values of coating thicknesses (a) and adhesive bond strength (b) of thermally sprayed (P1: Horizontal, P2: Flat, P3: Overhead) and additionally thermally sprayed sealed specimens](image)

In general, an increase of adhesive strength values (of approx. 2-3 MPa) could be determined in sealed samples in comparison to the thermally sprayed coatings. An abnormality for the evaluation of the adhesive strength after sealing was that the values of the sealed samples P1.3, P2.3 and P3.3 (Sealer with 40 %-thinner) were comparable to adhesive strength values of the thermally sprayed coatings or had the lowest values of all sealed samples.

### 3.2.2 Characterization of layers with metallography preparation

The thermally sprayed and the thermally sprayed and sealed samples were characterized using microscopically study methods (light microscope, scanning electron microscope with EDX-analysis) and the results were documented using microscopic images.

Thermally sprayed coatings (TS) showed a typical lamellar layer structure with little oxide streaks (grey, around the lamellae) and a relatively high roughness. Blasting material residue (corundum) was found on the boundary layer substrate.

Figure 3 shows a summary of the microscopic measurements of the coating thickness. The coating thicknesses of the thermally sprayed layers are relatively constant-
ly for the sample series P1 and P2 (exception P2.3) and with heavy fluctuations for the sample series P3 (value of 75 up to 135 µm).

The sealer had a more or less even effect depending on the layer resulting in lower thickness. Some micro cavities on the phase transition of thermally sprayed coating/organic layer were found. The infiltration depth of the sealer into the pores of thermally sprayed coatings could not be clearly determined in the light microscope images despite using fluorescent dyes. The layer thickness of the sealer decrease with diminishing binder content and increasing micaceous iron ore content (sealing class 1 with 5% thinner > sealing class 2 with 15% thinner > sealing class 3 with 40% thinner).

![Coating thickness of the samples [µm] (microscopical measurement)](image)

**Figure 3:** Values of coating thicknesses of the samples (microscopical measurements)

The SEM analysis of the layers shows clear topographical differences due to sealing the sprayed coatings. The unsealed samples showed oval shaped spray particles on its surface. The surfaces of the sealed sprayed layers were characterized by the micaceous iron ore particle as part of the sealer. Figure 4 shows example SEM-images of the layers.

![Example SEM-images](image)

**Figure 4:** Micrographs of the samples P3 (a: TS) and P3.3 (b: TS+ S with 40 % thinner) (SEM, surface)

The sealed layers showed different contents in iron (micaceous iron ore) and carbon (organic material) as well as different binders and micaceous iron ore contents (SEM-EDX). The sealer 3 (sealer with 40% thinner) showed the greatest iron content and
the lowest carbon content as well as the lowest binder content and the greatest micaceous iron ore content.

The SEM-EDX analyses of the surfaces showed that different Zn-content of the sealed samples indicates different coverage degrees of the thermally sprayed layers due to the seal. Since zinc was detected on all sealed surfaces, it is to be concluded that none of the thermally sprayed layers was fully covered with the seal. An increase of Zn-content was identified specifically for the sealed samples in the sealing class 3 (sealer with 40% thinner, P1.3, P2.3, P3.3) which indicates a low degree of coverage. The best cover of the thermally sprayed layers was determined for the samples of the sealing class 2 (P1.2, P2.2, P2.3).

3.2 Result of the study of the corrosion behaviour of the coatings

The coatings were evaluated at regular intervals during the corrosion exposure. White rust was already identified on all samples after 48h of exposure. After 360h of exposure in the test chamber, the formation of rather bulky corrosion products was observed (Figure 5).

The corroded surfaces of the samples were determined or the slightly/heavily corroded and uncorroded surface parts were calculated using photographs and an image processing program.

![Figure 5: Pictures of samples P2 (a), P2.2 (b) and determination of the corroded surface of samples P2 (c), P2.2 (d) after 360 h spray salt exposure](image)

(light corroded surface: red, not corroded surface: dark, heavily corroded surface: white)

For the sample system 1, the sealed samples P1.2 and P1.3 had a slightly light corroded surface and also slightly heavily corroded surface than the unsealed sample P1 (correlates with mass change).

The sealed samples P2.1, P2.2 and P2.3 showed significant reduction of the light corroded and the heavily corroded surface in comparison to the unsealed sample. In this context, the P2.1 showed the least corroded surface whilst the P2.2 and P2.3 had similar results (correlates with mass change).

For the sample system 3, the P3.2 showed less light corroded respectively less heavy corroded surface.

The lowest mass change (increase in mass) was determined for the samples P1.2, P1.3, all samples of the series 2 as well as P3.2 and P3.3. After 1000h of exposure, only white rust formation could be observed on all samples. After 1176h exposure all sealed layers showed in parts yellow discoloration.

Using the SEM analysis (EDX mapping), it became clear that all bulky corrosion products consist of zinc oxides or hydroxides (predominant) and aluminium hydroxides. The ratio between Zn/O and Al/O as well as increased chloride content showed
an increased formation of corrosion products for thermally sprayed unsealed samples (P1, P2, P3).

Figure 6 shows an example of SEM EDX element mapping of the cross section of P2.3 after 360h salt spray exposure.

Figure 6: Element mapping of the sample 2.3 (Sealer with 40% - thinner) after 360 hours salt spray exposure (SEM/EDX, the cross section)

The EDX-analysis of the cross sections of the tested sample showed a significantly higher chloride share for the unsealed sample in comparison to the sealed sample. An increase of the chloride content was indicated with increasing micaceous iron ore share/decreasing binder content for the sealed samples.

4 Conclusions

This paper studies the properties and corrosion behaviour of thermally sprayed and thermally sprayed and sealed coatings (in consideration of sealing variations, different spray parameters etc.). The result showed that thermally sprayed, sealed coatings have different coatings qualities and also different corrosion behaviour. For the studied samples, the best results of sealed samples were achieved by samples of the sealing variation 2 (organic coating material adding thinner of up to a 15% share). The results showed as a whole that the sealed layers had a better corrosion behaviour e.g. that the corrosion resistance of the layers was increased by sealing the thermally sprayed coatings.

Further studies, which in addition to the spraying position and the variation of the thinner share in the sealant examine variables such as the different thicknesses of thermally sprayed layers as well as the execution method (mechanical / manual) are also undertaken.

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5 References


[8] EN ISO 14919: Thermal spraying - Wires, rods and cords for flame and arc spraying - Classification - Technical supply conditions

