

CORROSION RESISTANCE OF ZINC-BASED SYSTEMS IN NaCl ENVIRONMENT

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Received: June 17, 2013

Abstract

VOTAVA JIŘÍ: *Corrosion resistance of zinc-based systems in NaCl environment*. Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis, 2013, LXI, No. 5, pp. 1487–1495

Metal components in engineering, industry and agriculture are subjects of degradation process influenced by corrosion which result in changes of mechanical characteristics. The current trend of anticorrosion protection is aimed at inorganic metal zinc-based coatings, such as zinc dipping which can be improved by duplex protection. This paper deals with two types of corrosion protection of steel components by zinc coating, first of which is produced by hot dip galvanizing, the other by Zn-Al spray.

Hot dip galvanizing was processed in working conditions; the Zn-Al coating was sprayed following the instructions of producer. It is a special aerosol with particles of Zn and Al sized approximately 5 µm. There have been processed the following tests: analysis of element structure, test of corrosion resistance in aggressive environment of salt spray according to ČSN ISO 9227, further measurement weight of applied coatings according to ČSN EN ISO 3892 and measurement of thickness of passivating coating. There was also made an analysis of coating tenacity on bending pin according to ČSN EN ISO 8401. Quality of applied coatings was evaluated following the metallographic scratch pattern.

hot dip galvanizing, zinc spray, renovation, cracks, corrosion

Corrosion is a gradual autogenous erosion of metals due to chemical or electrochemical reaction with the environment. This process can run in the atmosphere or in different gasses, in water as well as in other liquids, in ground and other chemical substances which are in contact with the material (Bartoníček, 1980). This erosion can be shown differently. There may occur a change in appearance, but also a total decay of a machine part (Dillinger, 2007).

Inorganic metal coatings produced by hot dip galvanizing or spraying melted zinc belong to high quality anticorrosion protection. Both of the above mentioned ways consist in passivation of the component by an oxidic layer formed by less noble metal whose electrical potential is lower than the potential of protected metal (Ambrož, 1990). Numerical values of standard potentials result from the comparison with potential of hydrogen electrode which was designated as zero (Ščerbejová, 1993). As the electrical potential of zinc is -0.76 and the electrical potential of iron is -0.44 , during the

electrochemical corrosion it results to a corrosion unit where zinc with more negative potential becomes an anode with oxidation processes. In that case it makes no difference what process of zinc-coating was used (hot dip galvanizing, hot dipping or metallization) as zinc passivates with its oxides (Svoboda, 1985).

Nowadays, also so called cold zinc-coating is being used. Cold zinc-coating is an application of zinc sprays where zinc accompanied by other anticorrosion elements is applied in the form of an aerosol on a component surface. This technology is being used mostly in renovation of badly zinc-coated surfaces. The applied coatings after a mechanical damage are able to produce a sufficient amount of corrosion products which are able to protect the base material (Trethewey, 1995).

MATERIAL AND METHODS

In general, the resistance of zinc coatings to the origin of microcracks during the shaping process is

very low (Votava, 2012). The aim of the experiment is to compare mechanical characteristics of hot-dip-galvanized coatings to a Zn-Al coating sprayed on base material. The individual analyses were made on samples with defined coating thickness and chemical composition.

Characteristics of zinc coating technologies:

- zinc dipping is a kind of anticorrosion protection formed by inorganic metal coating. Process of zinc dipping consists of the following steps: degreasing, chemical cleaning, flush, flux application, drying, dipping in melted zinc, cooling. One of the main factors influencing the thickness of the coating is the time of dipping in zinc bath.

For this experiment the dipping time was set for 100 seconds.

- Zn-Al spray is suitable as an anticorrosion protection of all types of metal bases. Zn-Al corrosion inhibitors can be even applied on partly corroded base and on impaired zinc coatings. These corrosion inhibitors on the base of acrylate resins with high percentage of zinc and aluminium in the base matrix are very often used in renovations and repairs. The inhibitor is resistant to temperatures up to 500 °C. Zinc sprays can be designated as successors of “metallization” (Matejka, 1989).

To samples of standardized size of 150 × 65 × 0.8 mm, there has been sprayed a layer of 85 µm.

There have been prepared sets of samples from each category and there were processed the following tests:

1. analysis of element structure of the metal coating,

2. determination of weight of applied coating according to the norm ČSN EN ISO 3892,
3. determination of the thickness of the passivating coating,
4. zinc coating analysis on bending mandrel according to the norm ČSN EN ISO 1519,
5. metallographic evaluation of applied coatings,
6. corrosion tests of the individual samples according to the norm ČSN ISO 9227 (salt-spray test).

Just to demonstrate the wide spectrum of usage zinc sprays in technical praxis, Zn-Al spray has been also applied on partly corroded base material.

RESULTS AND DISCUSSION

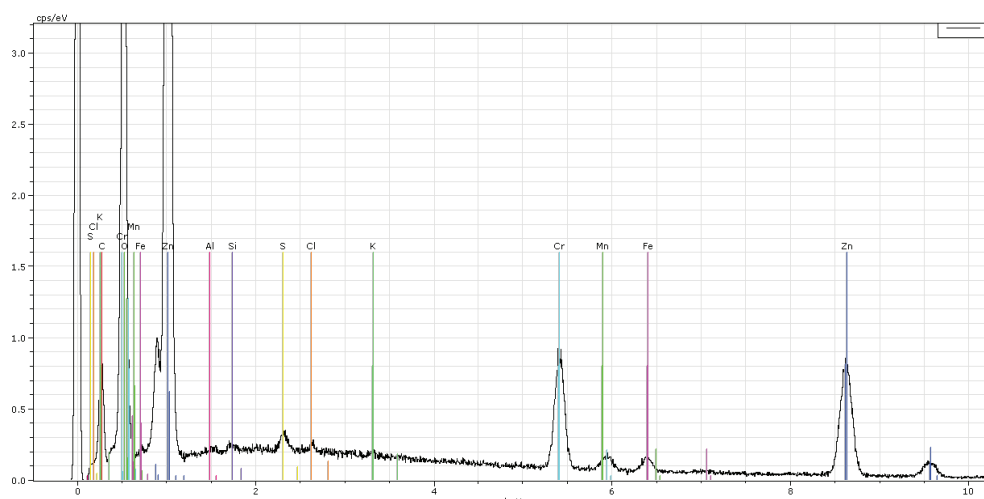
Analysis of elements structure of the metal coating

A scanning electron microscope VEGA II XMU (produced by the company Tescan) was used for the microanalysis of the elemental composition, in conjunction with energy dispersive microanalyser QUANTAX 800. The measurement of the elemental composition of a sample was performed on three different pads using the multiplication 100 times. The accelerating voltage equalled 15 kV. The readings are equal to mass concentration of 100%. The results of the chemical composition of the individual metal layers gained are presented in Tab. I and they show the average value obtained out of three measurements.

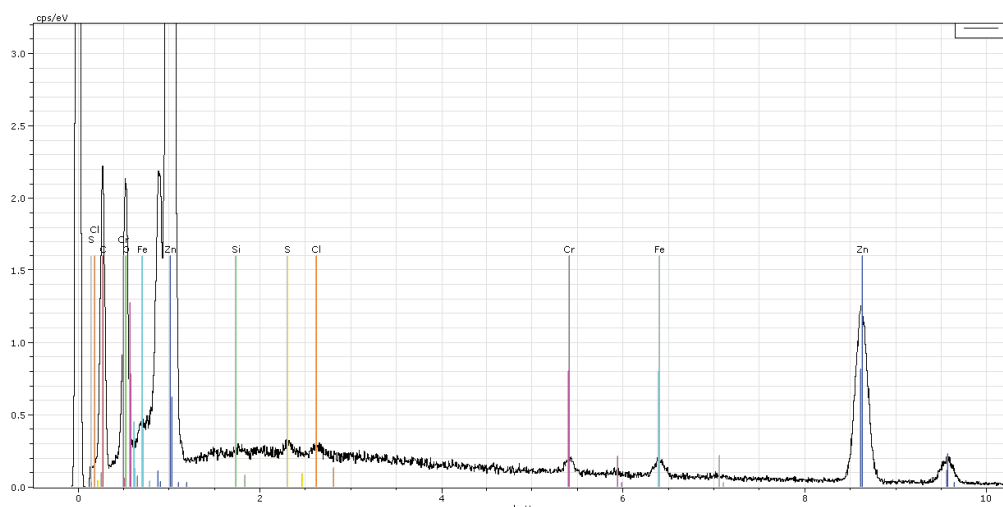
The quantitative analysis used the intensity of the line drawn by the individual chemical elements

I: Chemical composition of the tested anticorrosion coatings

Spectrum	Al [% _{mp}]	Si [% _{mp}]	Pb [% _{mp}]	Cl [% _{mp}]	Cr [% _{mp}]	Mn [% _{mp}]	Fe [% _{mp}]	Zn [% _{mp}]
Dipped zinc	0.41	0.89	0.07	0.27	0.18	0.15	4.12	95.27
Zn-Al spray	23.00	0.12	0.65	0.23	1.57	0.61	2.72	65.00



1: EDS spectrum of the dipped zinc



2: EDS spectrum of the metal coating Zn-Al

(see Fig. 1 and 2). The mentioned graphs serve the evaluation software as an input for the quantitative analysis.

Weight assessment using gravimetric method

The anticorrosion protection of zinc dipped samples depends on the amount of zinc coating applied to the base material. In order to analyse the weight of the zinc coating the procedure described in the norm ČSN EN ISO 3892 was used. It is a gradual decontamination of the applied coating from the base material.

Samples were cleaned and weighted before the test itself. Further, the passivation coating was being gradually decontaminated. At the laboratory temperature, the decontamination interval was set for 5 minutes, after which the samples were washed under the running water, dried and weighted. The whole process was repeated until a constant decrease of weight was reached. In order to measure the weight, there have been used laboratory weights

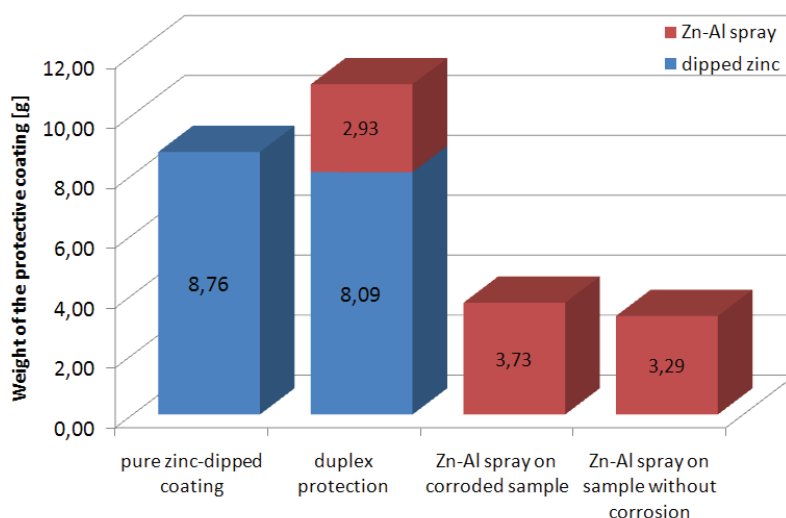
with the accuracy of 1 mg. The final value was computed as an average value of three readings.

In order to find out the weight of the Zn-Al coating a reverse process was used, that is steel samples has been measured before the application of the passivation coating, further after each spray application the samples were weighted. Weights of the individual coatings are depicted in Fig. 3.

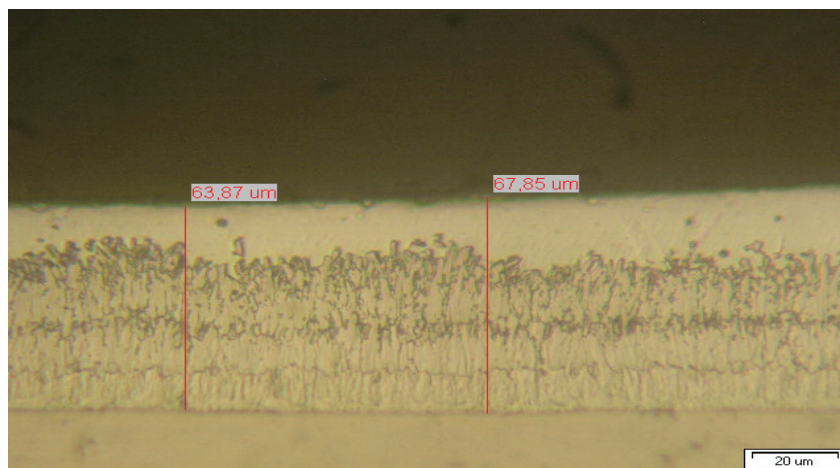
Assessment of the thickness of the anticorrosion coating

Thickness of the zinc coating is one of the most important factors influencing durability of the zinc coating. Based on their researches, the Association of Czech and Slovakian Zinc Works (Asociace českých a slovenských zinkoven) states, that depending on the environment the corrosion decrease is from 0.64–1.57 μm per year.

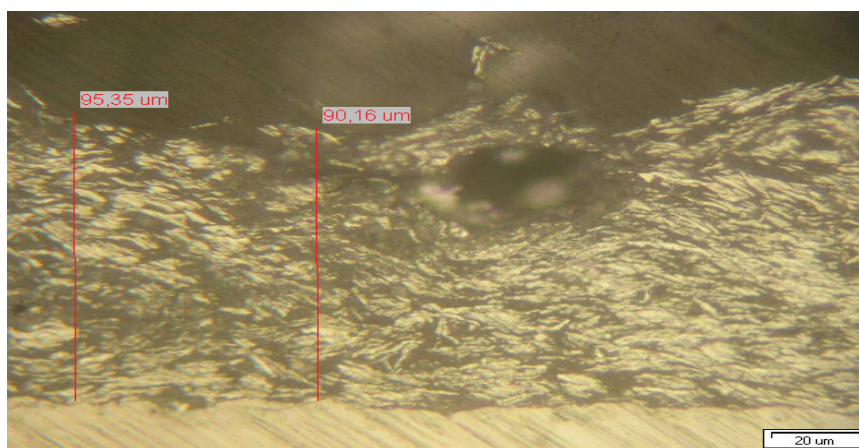
In order to measure the thickness of the passivation coating there were prepared metallographic samples. Afterwards, using the



3: Average weight of the applied anticorrosion coating



4a: Hot dipped zinc coating, magnified 400 times



4b: Zn-Al sprayed coating, magnified 400 times

computer programme analySIS there was read the value of the applied coating with the accuracy of 1 µm. To achieve objective readings, each layer was represented by three samples. Out of each sample 5 readings were obtained and arithmetic average was calculated. Structure and thickness of the coatings are recorded in Figs. 4a and 4b.

Bending test according to the norm ČSN EN ISO 1519

In general, ductile characteristics of zinc are rather low, and thus the zinc coating highly prone to cracks. This negative process can be outweighed by the so called “self-healing effect” of the whole system. Self-healing effect is defined as production of ZnCO_2 on a zinc coating which not only protects the zinc coating but also the base material from a further oxidation. (Votava *et al.*, 2012)

One of the ways to access the ductile characteristics of zinc coating is the bending test on a cylindrical mandrel. The coating is evaluated after bending on a mandrel with a certain diameter. This test can be processed also for heat-degraded coatings (Votava, 2009).

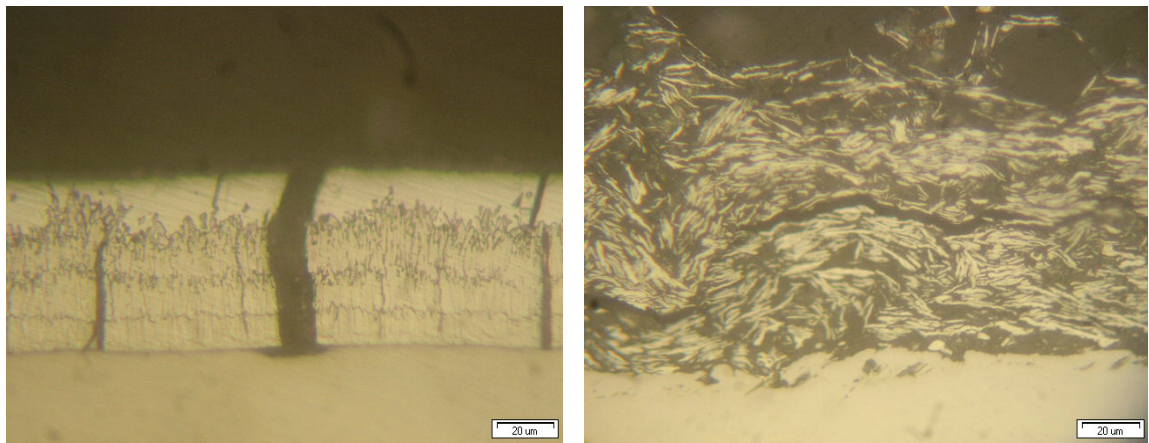
- Tested samples: there were tested steel sheets of the size $150 \times 65 \times 0.8$ mm. For the statistical reasons, there were used 3 samples for each mandrel, which means that there were tested 24 samples in total.
- The diameter of testing mandrels is 6, 16, 25 and 32 mm.

Hot-dipped zinc coatings perform thread cracks at any diameter of the mandrel. Sprayed coatings showed cracks only at the smallest diameter of the mandrel (6 mm). Mentioned cracks are depicted in Fig. 5.

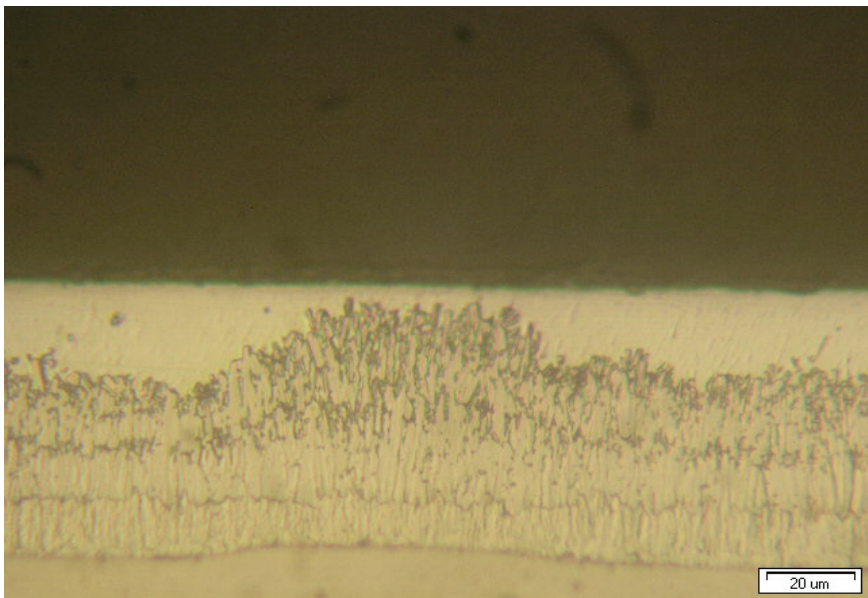
Metallographic evaluation of applied coatings

In order to prepare metallographic samples, methylmetaacrylate casting resin was used. Metallographic evaluation was processed on a metallographic microscope Neophot 2 and software analySIS for deduction of length parameters.

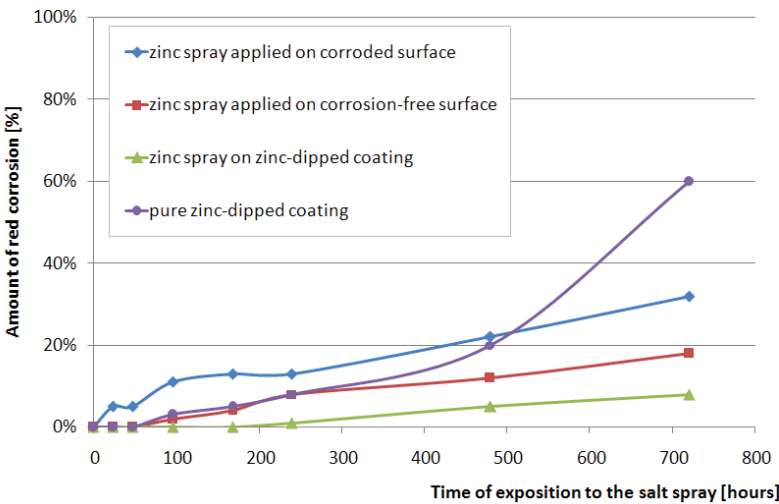
Chemical phases of zinc protective layer are determined by the technology of zinc dipping. Melting temperature of zinc and thus its usage for passivation coating on steel base is 420 °C; dipping time is 100–300 seconds which directly depends on



5: Crack in a zinc-dipped coating, after bending on 16 mm mandrel (left), cracks on Zn-Al sprayed coating after bending on 6 mm mandrel (right), both magnified 400 times



6: Zinc coating with “outburst”, magnified 400 times



7: Corrosion degradation of the individual anticorrosion protections

the weight of the whole machine part. During the dipping time, all surface iron ions actively diffuse the into zinc coating, which results into so called intermetallic phases (see Fig. 6), which subsequently lowers anticorrosion characteristics of the whole system and also worsens mechanical tolerance of zinc to cracks (Zmrzlý, 2003).

As it is apparent in Fig. 6, there may occur that the intermetallic phases grow to the surface of

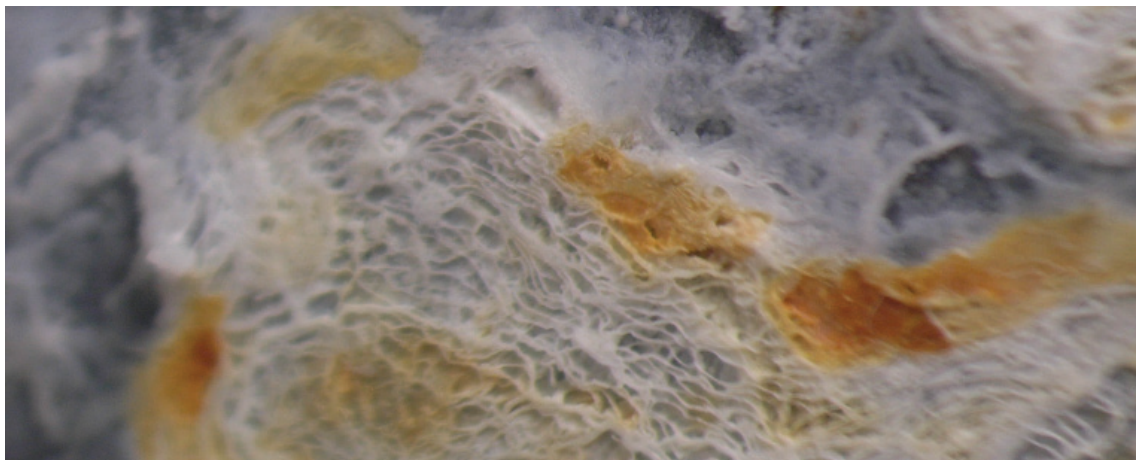
the protective layer. This phenomenon is called “outburst”.

Evaluation of anticorrosion characteristics in the salt-spray environment

The test of corrosion resistance of the individual systems of organic and metal coatings was processed by the standard method according to the processes of the norm ČSN ISO 9227 – salt-spray test. Salt



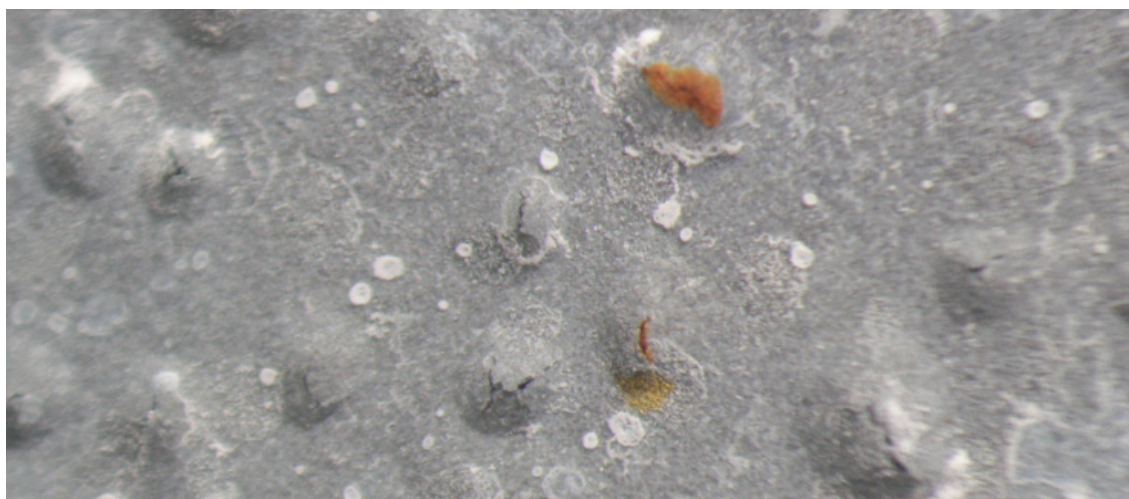
8a: Corrosion products of unprotected steel sample



8b: Point corrosion of zinc-dipped coating



8c: Corrosion of duplex protection – hot dipped zinc + Zn-Al spray



8d: Zn-Al spray applied on corrosion-free metal surface



8e: Zn-Al spray applied on corroded metal surface

8: Surfaces of the individual anticorrosion protection coatings after 15-day exposure in the salt-spray environment

spray chamber Liebisch, type S400M-TR was used for this experiment. Tested samples were sized $150 \times 65 \times 0.8$ mm.

Parameters of testing:

- temperature in the salt-spray chamber 35 ± 2 °C,
- concentration of the sodium chloride in a spraying medium 50 ± 5 g/l,
- pH value of the salt solution 6.5–7.2,
- the time interval was set for 1, 2, 4, 7, 10, 20 and 30 days.

CONCLUSION

Corrosion of metals causes the change of mechanical and physical characteristics of machine parts. In order to protect metal parts both inorganic and organic coatings were used (Tulka, 2005).

This paper is focused on analysis of corrosion degradation of coatings on the basis of zinc. There were compared two different ways of application

of zinc coatings: hot application (zinc-dipping) and cold application (using zinc sprays). In both cases, the anticorrosion protection depends on the ability of zinc to form passivating layer (Matejka, 1989). However, the current trend is represented by duplex protection which is a combination of inorganic and organic coatings (Votava, 2011).

The main goal of this paper was to compare the speed of corrosion degradation in the salt-spray environment. There was also analysed the weight and the thickness of the applied protective coating. Chemical composition was evaluated using the EDS method. Further test processed was the test of ductility using bending test according to the norm ČSN EN ISO 1519. There was made a metallographic analysis with the evaluation of cracks.

The lowest resistance to the salt-spray environment was shown by samples protected by zinc-dipped coating. It can be stated that after 30-day exposition to the environment of the salt spray,

red corrosion attacked the sample from about 60 per cent. Samples protected by Zn-Al spray performed about 20–30% of red corroded surface, duplex protection showed below 10% of corrosion attack.

Even though the duplex system performs the lowest corrosion attack, it can be stated that applied Zn-Al spray has a lower ability to reduce air humidity diffusing to the base material. This is apparent from the amount of zinc hydroxide released from the base zinc-dipped coating.

Ductility test according to the norm ČSN EN ISO 1519 has proved a low mechanical tolerance of zinc coatings to bending. Zinc-dipped coatings showed cracks in their whole cross-cut on all bending mandrels. Samples protected by Zn-Al were cracked

only when bending in the mandrel with the radius of 6 mm. The low mechanical persistence of these coatings is apparent.

According to the element analysis, there can be stated that the tested coatings contain also undesirable chemical elements, such as lead (Pb). This chemical element was especially observed in the zinc-dipped coatings.

Corrosion-protective coatings on the basis of dipped-zinc can be especially used in environments with lower corrosion assertiveness. Additive sprays perform a better corrosion resistance which is due to further added anticorrosive elements, aluminium above all.

SUMMARY

Corrosion is a world-wide problem. Corrosion causes not only a surface decrease of a material but also worsens the function of fitting components.

As it was already mentioned in the introduction, corrosion depends on the corrosion environment and the stage of air pollution. As the automotive industry is one of the main pollutants, the effort of designing engineers is to improve combustion process and lower the emissions to the environment (Veverka *et al.*, 2011). Corrosion aggressiveness can be noted along the roads – on bridge constructions and crash barriers.

This paper is focused on real evaluation of corrosion parameters of anticorrosion coatings on the base of zinc, which are one of the most common protections applied on steel parts along roads. One of the criteria was to compare anticorrosion protection of anticorrosion protection of Zn-Al spray in the environment of salt-spray. The producer states that the protected steel surface should bear at least 420 hours before the red corrosion origins. This spray was also applied on corroded surface and there was observed its passivating ability.

There was observed a higher production of zinc hydroxide on the samples protected by zinc-dipping. Even though the thickness of the coating was about 70 µm, after 720 hours of salt-spray test, red corrosion attacked the surface from 60 per cent. If there Zn-Al spray had been applied on corroded surface, than after 720 hours of testing such samples showed red corrosion on 30% of the surface. Samples with Zn-Al were corroded from 20 per cent. The best results were achieved by the so called duplex system which was attacked by the red corrosion from 10 per cent.

As it implies from the tests processed, the protection against inorganic coatings can be applied on a wide variety of steel machine parts. In order to increase the corrosion resistance, it is advisable to use a combination of more corrosion protective elements.

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