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ANTICORROSION PROTECTION OF STRENGTH BOLTS

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Abstract

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Corrosion damage may, from the technical point of view, cause changes in mechanical and physical characteristics in particular, at the same time it may also cause changes in surface geometry. These aspects are likely to manifest themselves in all steel parts. The presented study looks at corrosion protection in bolts and bolt connections protected by metal coating based on zinc.

Four different types of passivation, easily accessible on the Czech market, have been selected for this experiment. They are as follows: first, galvanic plating using white zinc; second, galvanic plating using yellow zinc; third, hot dip galvanizing; fourth, specific type of plating using the technology Dacromet 500 LC. In order to compare the given parameters there have been selected a unified M bolt size of 8 × 30 mm.

The experimental part of this study can be further divided into two phases. The initial phase puts stress on the exact specification of the protection layer, namely, the analysis and establishment of the elemental compositon contained in the given coating, its microhardness, weight and thickness. The second phase of the experiment analyses the results of tests according to the norm ČSN ISO 9227 (Salt Fog Test) and ČSN ISO 6988 (Sulphur Dioxide Test). With the tests we have concentrated on the initial stages of corrosion degradation and its overall process.

corrosion, zinc plating, analysis, bolt, elemental composition

Metals, plastic and furhter types of materials are all subject to corrosion (Průšek *et al.*, 1985). Quality anticorrosion protection guarantees a longer working life not only to machines and machinery equipment, but also to the metallurgical material itself (Bartoníček, 1966). The expected costs of anticorrosion protection equal in some cases up to 10% of the product price (Porter, 1991). Engineering companies invest considerable amount of finance into optimalizing processes and anticorrosion protection. If corrosion occurs over the overall functional surfaces of the associtaed components, the entire system will be degraded (Ščerbejová, 1993).

Metal layers application is the most frequently employed type of anticorrosion protection in bolt connections, vast majority being the zinc coating. This type of coating has its decorative as well as functional qualities. One of its greatest advantages is its so called "self-healing effect" when the protective coating is able to create a sufficient amount of corrosion products (after having sustained mechanical damage) which further on protect the base material (Kending, 2003).

Such anodic protection follows the principle of ion circulation and production of zinc carbonate (Marder, 2000). However, in an aggressive environment with an increased amount of sodium chloride ions, the corrosion resistance of zinc coating drops down significantly.

MATERIALS AND METHODS

For the experiement several types of anorganic metal protection were chosen, they were the zinc coatings applied using different technologies. A unified size of bolts to be tested was M 8 × 30. The coatings subject to testing showed the following characteristics:

- galvanic zinc plating is a type of electrochemical plating using one-direction current and a negative electrode, ie. cathode, the cathode's surface emits metal coating (Svoboda *et al.*, 1985). It is right here where to put the objects/items subject to plating. The compostion of the plating layer is substantially influenced by the anode material and the electolyte. The samples subject to testing which were produced used the method above belong to the cathegory of white and yellow zinc (Bartoníček, 1980).

- hot dip galvanizing is a method which we use to create a protection layer as thick as several dozens µm (Dillinger *et al.*, 2007). In bolt conjuctions it is necessary to preserve the profile of the bolt thread, therefore so called centrifugal zinc plating is being used. The surface created using this technology does not show such a degree of metallic luster as when using the galvanic plating, though, and simultaneously it leaves the surface much rougher (Pejčoch *et al.*, 2006).
- inorganic zing coating can be represented by a classical example of its kind – Dacromet technology. It is based on the technology of inorganic carrier particles, onto which particles of zinc and aluminium bind. These particles have been passivated in advance in order to attain higher surface brightness. At the same time hydrogen brittleness is supressed and, and thus, the risk of surface cracks is eleminated.

Based on the above mentioned cathegories sets of samples were produced. These samples were subject to the following procedures:

1. elemental composition analysis of the metal layer composition,
2. weight assessment of the passivation layer in compliance with the norm ČSN EN ISO 3892,
3. thickness assessment of the passivation layer on the bolt thread profile,
4. microhardness measurement in the individual passivation layers,
5. corrosion tests of the individual samples in compliance with the norms ČSN ISO 9227 (Salt Fog Test) and ČSN ISO 6988 (Sulphur Dioxide Test).

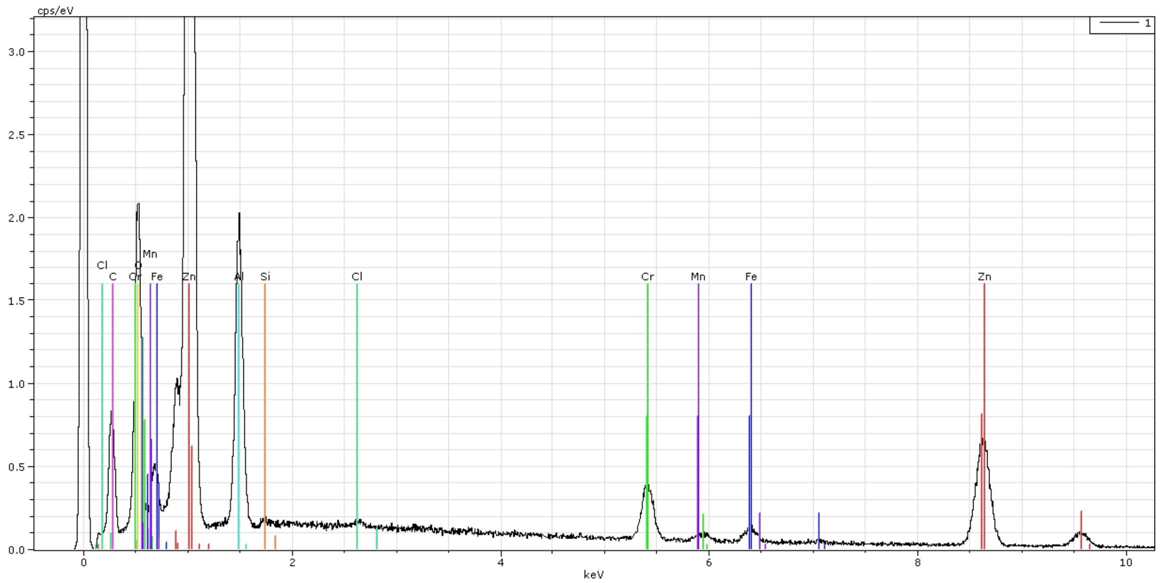
RESULTS AND DISCUSSION

Elemental composition analysis of the metal layer

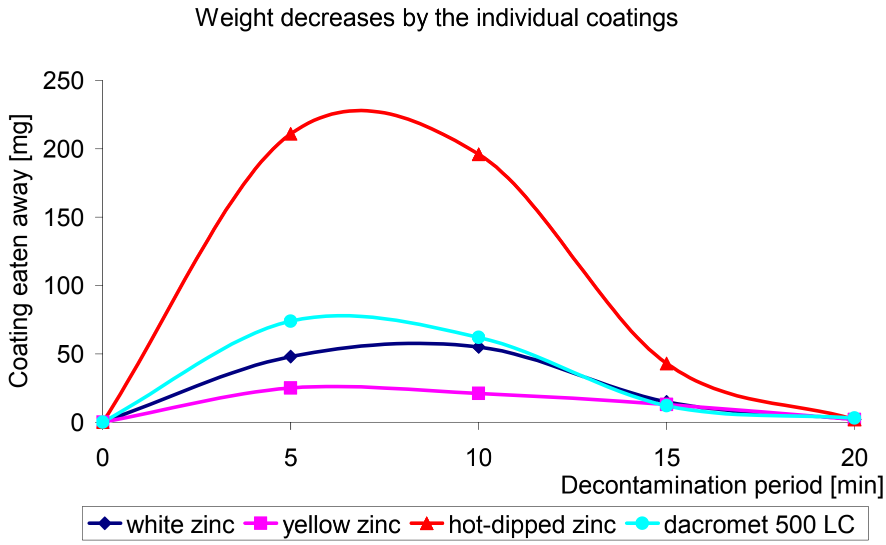
A scanning electron microscope VEGA II XMU (produced by the company Tescan) was used for the microanalysis of the elemental composition, in conjuction with energy dispersive microanalyser QUANTAX 800. The measurement of the elemental composition of a sample was perfomed on three different pads using the multiplication 100 ×. The

I: *Chemical composition of the tested anticorrosion layers*

Spectrum	Al [$\%_{mp}$]	Si [$\%_{mp}$]	S [$\%_{mp}$]	Cl [$\%_{mp}$]	Cr [$\%_{mp}$]	Mn [$\%_{mp}$]	Fe [$\%_{mp}$]	Zn [$\%_{mp}$]
White zinc	0.34	0.18	0.37	0.27	1.28	0.15	2.12	95.27
Yellow zinc	0.33	0.27	0.65	0.30	15.57	0.61	2.72	79.18
Hot dipped zinc	2.14	0.90	0.34	0.29	0.88	0.25	4.10	91.01
Dacromet 500 LC	13.30	0.39	0.08	0.36	7.19	0.48	3.12	75.06



1: *EDS spectrum of the metal layer (yellow zinc), for results of chemical composition see Tab. I*



2: *Weigh decrease of anticorrosion layer under the measurement interval of 5 minutes*

measurement was made on a sample surface. The accelerating voltage equaled 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.

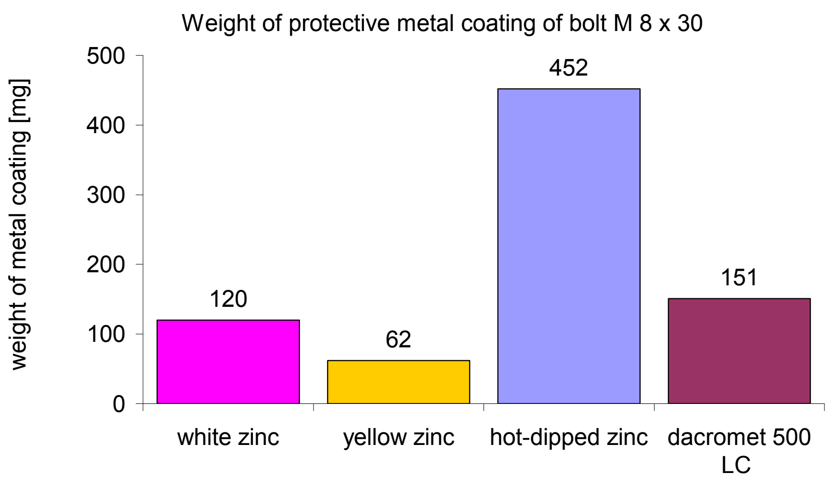
The quantitative analysis used the intensity of the line drawn by the individual chemical elements, see Fig. 1, which serve for the evaluation software purposes.

Weight assessment using gravimetric method according to the norm ČSN EN ISO 3892

The above norm establishes the exact proceedings while finding out the weight of the protective layer applied onto a surface. It lies in a gradual decontamination of the metal layer out of the surface of the base material. The final reading is given as the average value out of three measurements made. Weight was established using laboratory scale with precision to 1 mg. Prior to the test, the samples were cleansed and weighed to be subject to the gradual decontamination of the passivation layer. The decontamination interval was established as 5 minutes under laboratory temperature. After the interval had passed, the samples were cleansed with running water and weighed again. The whole process was repeated until a constant decrease was reached. The results of the weight decrease are shown in Fig. 2.

The solution which was used to decontaminate the passivation layer was aqueous solution containing in one litre of distilled water 200 g of CrO_3 and 10 g of $BaCO_3$.

During the initial intervals of the decontamination cycle, there can be seen a rapid derease in metal layer. The overall decontaminated weight of the protective layer after a 20-minute interval is shown in Fig. 3.



3: *The overall weight of metal layer*

Assessing the thickness of the metal layer

Passivation layers applied through the galvanic metal application reach only limited values. In more detail, they equal several µm or a few dozens of µm at the most. A precise measurement of the layer thickness using a non-destructive method is highly difficult, in particular when dealing with the central part of the bolt thread diameter. Due to this a metalographic cut was made of the individual samples, the readings obtained were deducted using the metalographic preparation. To achieve objective readings, each layer was represented by three samples. Out of each sample 5 readings were obtained and arithmetic average was calculated.

In Figs. 4 and 5 the different thickness of the layers can be well observed. The pictures show the central segment of the bolt thread where there is no threat of inappropritate metal layer application, as opposed to the tip of the bolt thread.

As can be seen from Fig. 6, the hot dip galvanizing guarantess a considerable thickness of the protective layer.

Microhardness of the metal layers tested

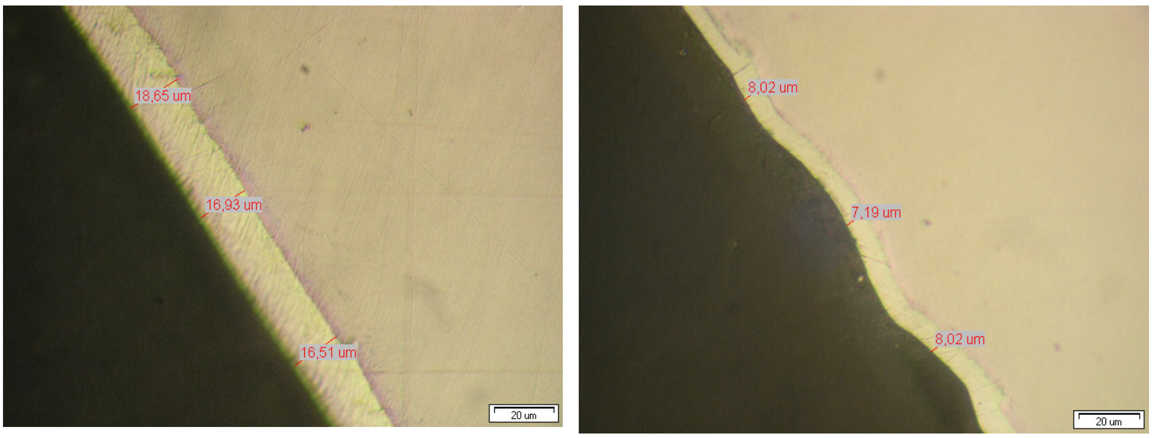
Microhardness may be crucially influenced by chemical composition of passivation substrate as well as by the application method of the metal protective layer. In some materials it is possible to improve corrosion resistance in the whole system by increasing the material hardness.

Microhardness was measured with Hanneman microhardness device, which is a part of a metallographic microscope Neophot 2, using a standard Vickers method in the frawework of ČSN EN ISO 6507-1. A diamond-tipped cone of 136° using the force of 0.9809 N is indented into the material. According to the length of diagonals the HV microhardness value is read. The evaluation was made using DP-Soft100 software.

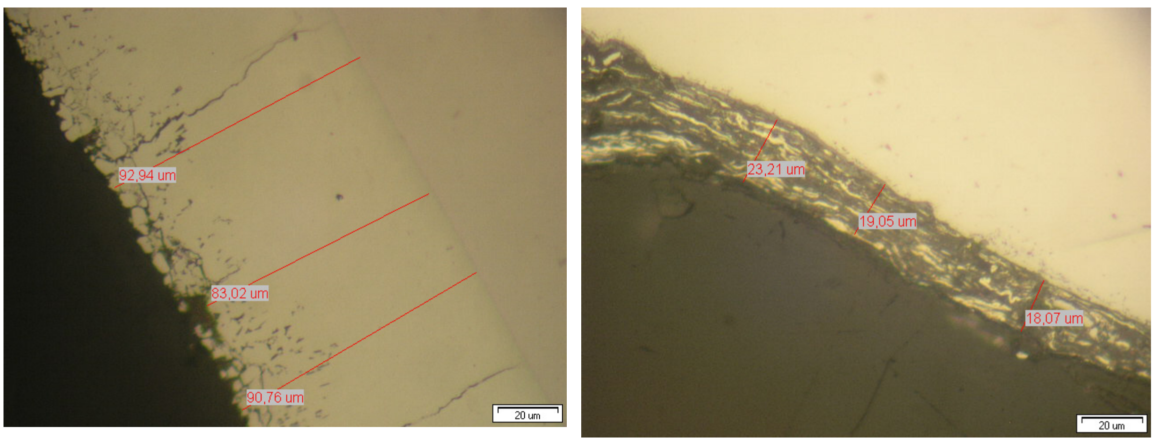
The measurement was undertaken using three samples for each metal layer. Five readings were obtained based on each sample as the basis for an arithmetic average. The individual microhardness readings are shown in Fig. 7.

Anti corrosion resistnace of the individual metal protective layers

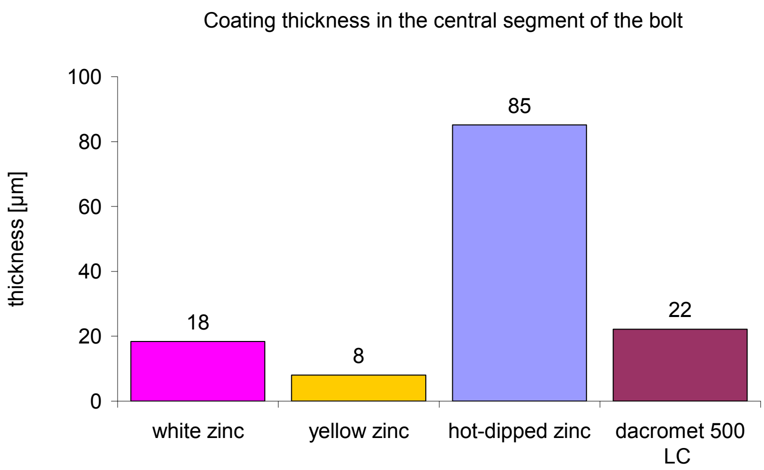
A corrosion resistance test of the bolts and different metal protective layers were performed using the standard method under conditions of corrosion chambers NaCl and SO_2.



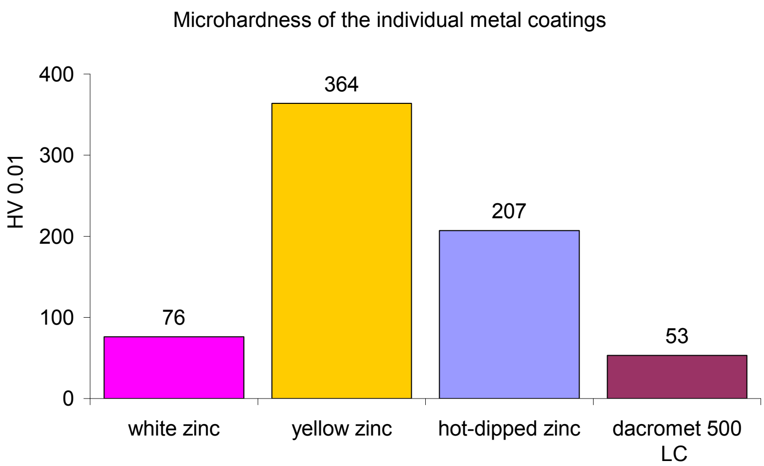
4: *Passivation layer thickness in white zinc (left) and yellow zinc (right), magnification 400 ×*



5: *Passivation layer thickness in hot dip galvanizing (left) and Dacromet 500 LC (right), magnification 400 ×*



6: *Protective metal layer thickness*



7: *Individual metal layers and their thickness*

Salt Fog Test in compliance with ČSN ISO 9227:

- temperature 35 ± 2 °C,
- sodium chloride concentration 50 ± 5 g/l,
- pH of the sprayed solution 6.5 to 7.2,
- testing time was set in intervals according to the gradual corrosion process and daily visual assessment.

Sulphur Dioxide Test in compliance with ČSN ISO 6988:

- test chamber tempretaure 40 ± 3 °C,
- one test cycle equals an 8-hour exposition to aggressive corrosion environment including a 4-hours ventilation of the test chamber,
- amount of sulphur dioxide per one cycle 0.2 dm^3,
- test results based on visual assessment.

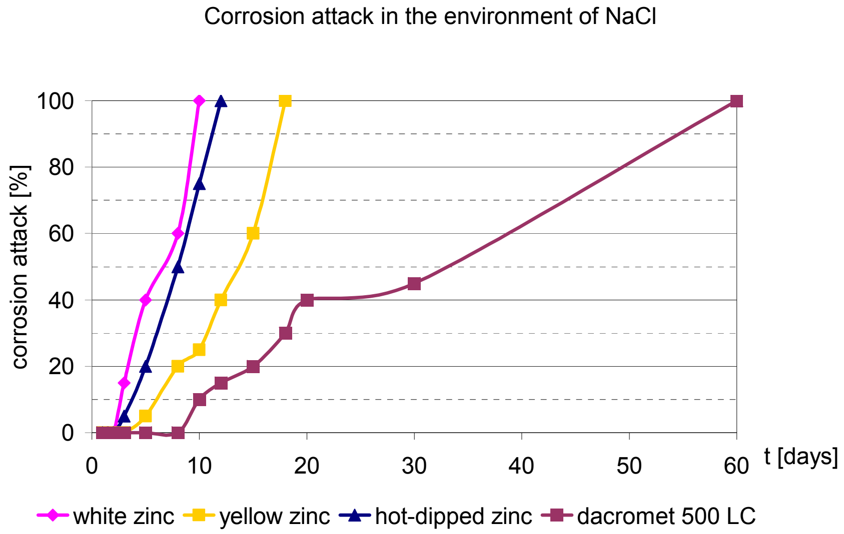
Groups consisting of 5 samples of each material were given to both of the testing chambers. In order to guarantee corrosion influences on the whole bolt profile, samples were placed into a special preparation. Samples have been continuously visually evaluated and a photodocumentation was made. The overall test contour is illustrated by Figs. 8 and 9.

Following the results of the accelerated corrosion tests, a low resistance in zince protection layers in NaCl environment is obvious. How fast the degradation is not directly dependent on the thickeness of the zinc layer, but undoubtedly it depends on the chemical composition.

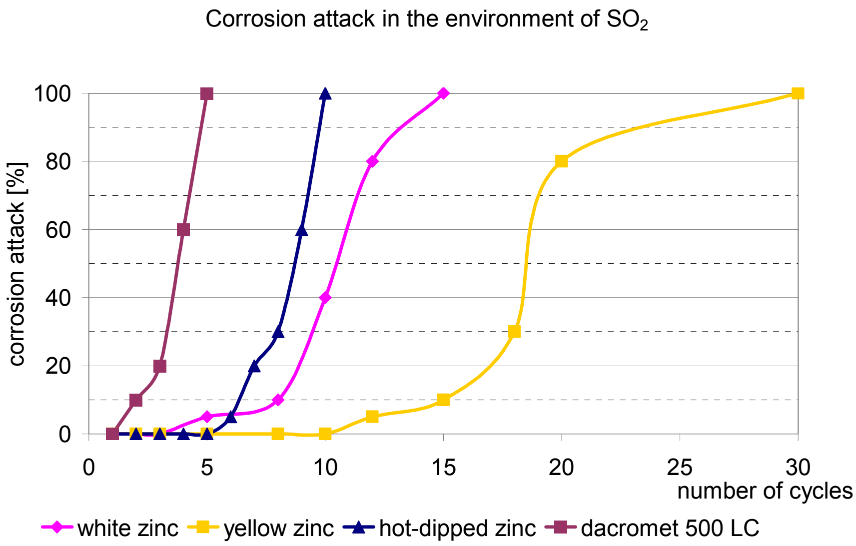
Difference in degradation processes documented in 2 different environments are well seen in Fig. 10, which shows white zinc with expositon of 2 days in salt chamber compared to exposition to SO_2 chamber. Under NaCl the degradation show signs of zinc transformation into by-products of zinc hydroxide, whereas under SO_2 conditions decontamination and overall loss of the passivation layer up to the base material is observed.

CONCLUSSIONS

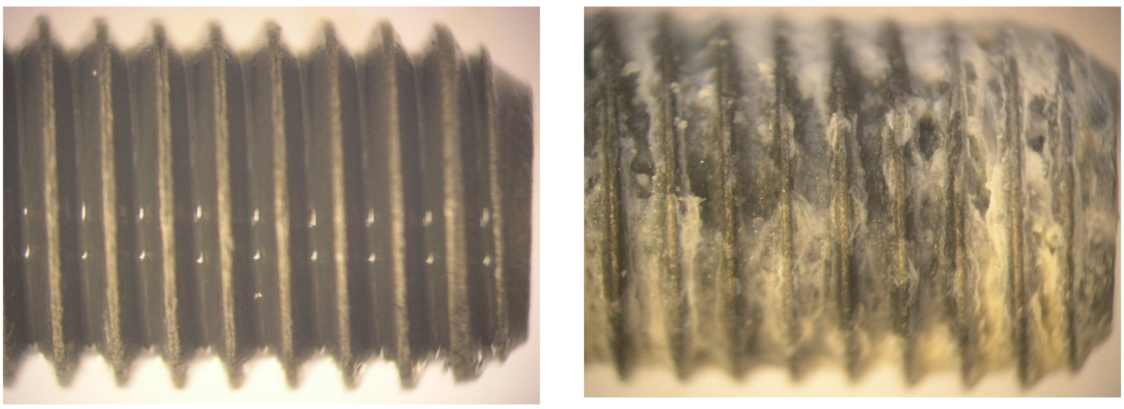
Corrosion of bolt conjuction represents a world-wide problem. New stategies in developing passivation layers are constantly under way. Moreover, ecological aspects of production as well as disposal of galvanic baths are subjects of discussion.



8: *Corosion test degradation in NaCl environment*



9: *Corosion test degradation in SO_2 environment*



10: *Corosion degradation under SO_2 (left) compared to NaCl (right)*

Among other, this contibution explores monitoring of corrosion resistance of metal layers based on zinc. In particular, the process of degradation during accelerated corosion tests under salt fog and sulphus dioxide envirionment. Furthermore, the microhardness values, overall weight and thickness of the applied substate have been analysed. Using the EDS method chemical composition of the individual protective layers has been evaluated.

The highest corosion resistence has been performed in bolts which used galvanic zinc plating with yellow zinc, which constituted 16 $\%_{\text{mass percentage}}$ of Cr of the protective layer. This element provides to the layer increased microhardness values, which reached cca 360 HV.

The thickness of the layer applied (the centre shaft of the bolt) was only cca 10 μm, which points at a very short period of galvanic bath immersion. The overall weight of the substrate equals then cca 62 mg. The beginning of the red corosion degradation started to emerge after a 5-day exposition to the environment of NaCl, when exposed to SO_2 the corrosion started to appear afer 12 days. Total degradation of 100% was observed on the 18th day of the test under NaCl conditions and on the 30th day under SO_2 conditions.

Passivation protection created through hot dip galvanizing has been evaluated as having extremely positive results. The mass of the protection layer was cca 85 μm and it guarantess a high quality „self-healing effect“. Based on the EDS analysis, the protection layer mostly consists of pure zinc, including cca 2.2 $\%_{\text{mass percentage}}$ of aluminium, too. The overal weight of this layer in the M 8 × 30 bolt equals 452 mg on average. The red corosion appeared on the third day when exposed to NaCl and on the tenth day when exposed to SO_2. The test was completed on the twelfth day after the exposure to NaCl and the twentieth day after the exposure to SO_2 when the samples already showed signs of an overall degradation by the red corosion.

Another subject to testing was Dacromet 500 LC, a layer suited to extremely aggressive conditions being used for strength bolts of types 8.8 to 10.9. Due to its microhardness and metalographic cut the layer constitutes by large a very porous layer, whose primary inhibitation quality is the ability to create a passivation layer among the lamelas of the protection layer. It is the value of microhardness that suggests the porous character of the layer; it reaches around 50 HV.

The analysis of chemical elements involved indicates the combination of Al, Cr and Zn. Corrosion tests (which did not suggest any increased value of white corosion) reliably showed a possible future use of this protection layer in automotive industry, namely to protect vehicle chassis. Tenth day of exposition under NaCl conditions is the beginnig of corosion process, the test itself took 60 days.

The worst corosion resistance was observed in the bolts with white zinc. The thickness of the protection layer was around 20 μm for the individual samples, which corresponds to the 120 mg of zinc applied. The elemental analysis proves that the protection layer is composed of 95% by pure zinc. The red corosion process started already on the day 3 under NaCl conditions and on the day 5 under SO_2 conditions. Since the process was very fast, the test was terminated on the day 10 for the NaCl conditions, and on the day 15 for the SO_2 conditions. All these tests witnessed a total destruction of protection layer.

SUMMARY

In vast majority of cases bolt and bolt conjuction protection is based on metal protective layers application. It is due to the preservation of the functional qualities of the conjunction mechanism – there cannot be applied a massive layer of anticorosion substrate in between the bolt and its nut.

This study focuses on a realistic assessment of the mechanic parametres of the protection layer in strenght bolts, size 8.8 up to 10.9. The pace of the degradation under accelerated corosion tests has been monitored, as well as the onset of red corosion process.

The fundamental parameter has been the analysis of the elemental composition of the individual protection layers. It is due to the crucial fact that the combination of the easily passivated elements (withing the protective layer) constitutes a determining influence on the corosion process. The samples tested using the yellow zinc proved this aspect undoubtedly. The protection metal layer which contained 15.57 % Cr showed a resistance increase by 100% when compared to white zinc (here zinc on its own makes for 96% of the protection substrate).

The hot dip galvanizing process enables to create a substrate protection layer up to 90μm thick. This layer also guarantees high quality passivation characteristics of the base material, although it may be exposed subtle cracks, as seen in Fig. 5. In such cases, the so called "self-healing process" is triggered.

Strength bolts 10.9 with Dacromet 500 LC protection coating demonstrated outstanding results under NaCl conditions. As a result, this kind of protection is recommended for conditions characterised by an enhanced amount of salt.

Nevertheless, the standards of ČSN ISO 6988 under SO_2 conditions has been complied to proving a complete inability of the layer to protect the base material. Unavoidable, it has been demonstrated that the layer is not universal in its application.

It is one of the foremost priorities of the contemporary research to engage in all possible combinations of chemical elements in metal protection layers and their applications.

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