

QUANTIFICATION OF CORROSION ACTIVITY ON HDG STEEL SHEETS DURING CYCLIC DIP TESTS IN CLASSICAL AND ECOLOGICAL SALT SOLUTIONS

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Abstract

The paper is focused on the part of complex work dealing with verification of functionality of non-destructive technique of electrochemical noise applied on HDG steel sheets samples with different surface treatment, namely on samples to be treated with Cr³⁺, anticorrosion oil and non-oiled and non-passivated ones. Besides monitoring of quality of surface treated zinc sheets (activity/passivity) by ENA technique an extension of corrosion deterioration was quantified gravimetrically after 3, 15, 22 and 30 days of exposure in 3 % NaCl, 3% ecological salt mainly composed of MgCl₂, CaCl₂ and condensation chamber. Corrosion products were observed with support of SEM microscopy with EDX analysis.

Keywords: corrosion monitoring, electrochemical noise, activity, zinc surface

1 Introduction

It is well known that increased caution in various kind of industry is focused on corrosion problems and corrosion protection of surface treated metallic materials. The consequences of corrosion in automotive industry thus should be revealed before long-term testing of car body components, eventually first visible failures of inadequate combination of engineering parts caused problems during final phase of big developer's projects, even before inspection. For that reason, it is justified the interest in new approaches in corrosion monitoring techniques [1,2,3,4]. Application of modern corrosion monitoring methods served for shorter time needed for corrosion testing, for faster reaction on solution of occurred problems caused by corrosion aspects. The ability of evaluation of actual quality of coatings from the point of view of safe field application is very important. It is sufficient and more and more widespread also to forecast lifetime of materials. The current trend is mainly industrial inquiry for non-destructive monitoring of corrosion. Besides visual inspection, laboratory tests is still needed for verification. The added value of monitoring in terrain is that it helps for fast and relatively simple control in application environment with output in the form of detection of quality of surface treated material. At the same time it allows to determine defect free state, state with high passivity, low activity or high corrosion activity, which could lead finally to the failure of the protected system.

Electrochemical noise methods (ENA) using no contact to the substrate arrangements (NOCS) [5,6] is one of suitable corrosion monitoring approaches and helps to detect a corrosion resistance of zinc coatings or final paints. The noise resistance' is defined as the ratio of the standard deviations of the potential noise and the current noise between two identical working electrodes which are linked by a zero resistance ammeter (ZRA). The noise resistance has been used considerably, recently, in the research of corrosion phenomena and it is often found in literature to be equivalent to the polarization resistance [7,8]. It has been mathematically proved and empirically correlated to the polarization resistance in order to calculate the corrosion rate [9]. Furthermore it has been suggested that certain parameters derived from the statistical analysis of electrochemical current noise data such as the localization index (LI) provide information about corrosion mechanism [10,11] or special statistical treatment of both measured potential and current noise cover state of passivity of metallic surface[12,13].

During corrosion testing the original application environment is replaced by electrolytes with different aggressivity simulated field application such as atmospheric acidic electrolyte, e.g. simulated acid rain solution (SARS), classical technical salt – NaCl, ecological salts on the basis of MgCl₂, CaCl₂ or environments simulated cyclic temperature and humidity changes (condensation chamber, VDA tests etc.) [14].

2 Material and experimental methods

Testing was performed on hot dip galvanized steel sheets (HDG) with additional anticorrosion treatment, with passivation, passivation free with dimension of 100 x 120 mm. Three types of samples were used:

- Alfa – HDG steel sheets with thickness of 120 g.m⁻² of Zn coating, roughness 1.6 µm and 0% of Fe contain in Zn. Surface was non-passivated one with presence of anticorrosion oil.
- Gamma – HDG steel sheets with thickness of 120 g.m⁻² of Zn coating, roughness 1.4 µm and 12.6% of Fe contain in Zn surface. The surface was non-passivated and non-oiled.
- GI – HDG steel sheets with thickness of 100 g.m⁻² of Zn coating and passivated with Cr³⁺.

Three types of simulated electrolytes were used in experiments:

- 3% NaCl – simulation of solution served for technical service on roads in winter seasons.
- 3% solution of ecological salt solution on the basis of MgCl₂ and CaCl₂.
- Condensation chamber for accelerated testing of corrosion resistance under cyclic conditions where temperature and humidity is changing. E.g. VDA tests are very specific and differ for each automotive company in temperature and humidity time interval. During this kind of test cyclic achievement of the dew point is simulated, which caused condensation of water with presence of salt. Thus create the most suitable environment with maximum rate of corrosion phenomena – under thin layer of surface electrolyte.

2.1 Corrosion dip tests

Corrosion dip tests of hot dip galvanized structural steel was performed according to STN EN ISO 11130:2011 [15]. In the dip test, the parts are intermittently immersed in salt water solutions

mentioned above – 3% NaCl, 3% ecological salt solution with consecutive observation of corrosion resistance. According to the standard determined dip/drying was performed with 1000 cycles. The samples hang out during exposition on clamp holder made from isolated wires with assured clear distance ahead to be sure that no reaction between them occurred and no contact to bottom and wall taking place. At the same time the level of electrolyte do not decrease and was added continually during evaporation.

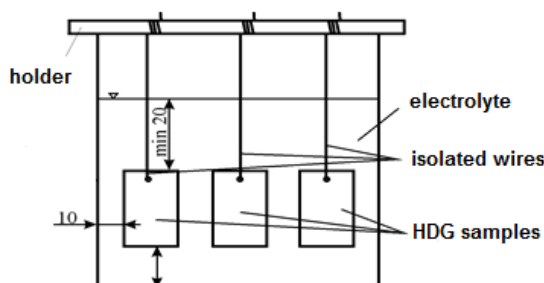


Fig.1 Schematic arrangement of corrosion dip test according to Chyba! Nenašiel sa žiaden zdroj odkazov. EN ISO11130:2011

2.2 Electrochemical noise measurements

Electrochemical noise analysis with no contact to the substrate arrangement (ENA-NOCS) was chosen for non-destructive measurements (Fig.2). The plastic sensor with two holes was located on the sample, filled with measurement solution. Reference electrodes were embedded within holder and attached to the sensor. The potential and current noise were measured using high sensitive digital multimeter KEITHLEY and data were evaluated by LabView [16].

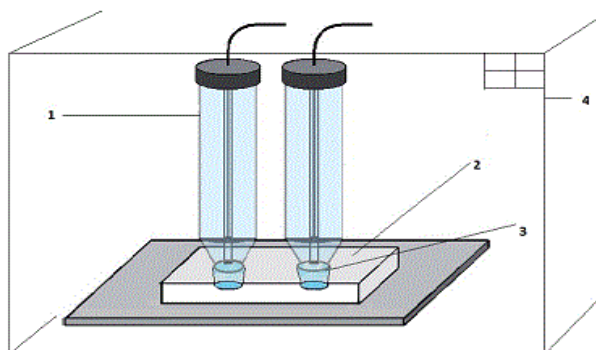


Fig.2 Sensor for measurement of ENA NOCS 1–electrodes, 2–metallic sample, 3–plastic sensor, 4–Faraday cage

3 Results and discussion

The output of non-destructive corrosion monitoring using ENA-NOCS setup is effective determination of activity/passivity of coatings with very high sensitivity. The results from measurements is shown in table 1. It was found out that very active state of corrosion has R_N values about $k\Omega \cdot cm^2$, for medium and low corrosion activity (e.g. for samples exposed to

outdoor non-polluted atmospheric conditions) R_N values range between hundreds of $k\Omega.cm^2$ and $M\Omega.cm^2$. Very low corrosion activity of zinc coatings under organic coatings, lacquer or multi-component paint could reach more than $M\Omega.cm^2$, high quality of coatings has R_N in $G\Omega.cm^2$.

From the results in Table 1 it is apparent that alfa HDG samples (non-passivated) were in active corrosion during whole exposition in 3% NaCl, which reveal by very low R_N values. Nevertheless, after 22 days R_N values were unable to detect by non-destructive technique caused by high mass losses of zinc, destruction of zinc coatings and occurrence of iron substrate steel. This fact was observed by SEM microscopy with EDX analysis (Fig.6).

On the other hand, alfa HDG samples exposed to ecological salt solution were passivated by suitable corrosion products with effective protection where relatively high R_N of 215 015 $\Omega.cm^2$ was obtained.

R_N values for HDG samples exposed in ecological salt solution and condensation chamber was very close to R_N values as for as supply zinc coatings. R_N values lower than 500 $\Omega.cm^2$ were reached for zinc coatings exposed in 3% NaCl solution after 30 days of exposition and that is why zinc coatings completely lost passivation functionality.

Table 1 R_N values from corrosion monitoring measurements using ENA

material/ exposure	as supply state R_N [Ohm. cm^2]	72 hours R_N [Ohm. cm^2]	360 hours R_N [Ohm. cm^2]	720 hours R_N [Ohm. cm^2]
ALFA1 (3%NaCl)	1611	1226	51 802	< 500
ALFA2 (3%ECO salt)	1611	590	6 721	215 019
ALFA3 (Condensation chamber)	1611	11 434	249 411	114 454

The gravimetric analysis of hot dip galvanized steel samples after exposure in 3% NaCl solution are shown on Fig. 3, 4, 5. The minimal mass losses of zinc coatings was reached after 30 days of exposition by gamma HDG sample, which contain 12.6% Fe in Zn coating. The maximum mass losses were detected on alfa HDG samples, non-passivated ones. The gravimetric analysis together with scanning electron microscopy with EDX analysis (Fig.6, 7, 8) were supporting methods only, helping to verify functionality and results obtained from non-destructive corrosion monitoring technique based on electrochemical noise.

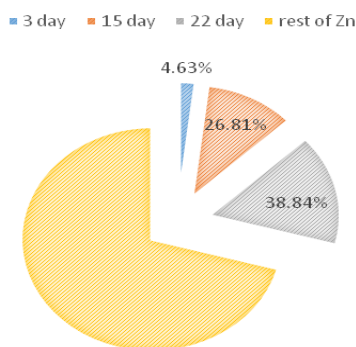


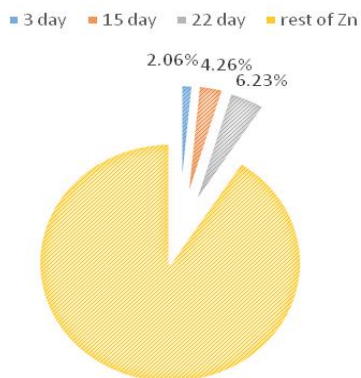
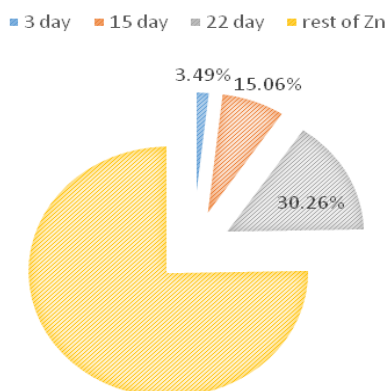
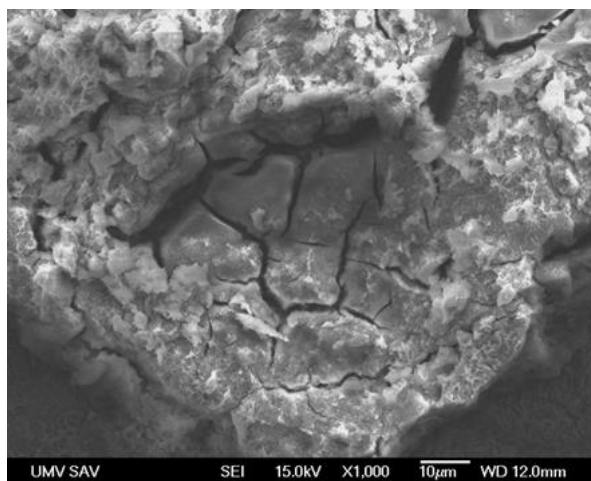
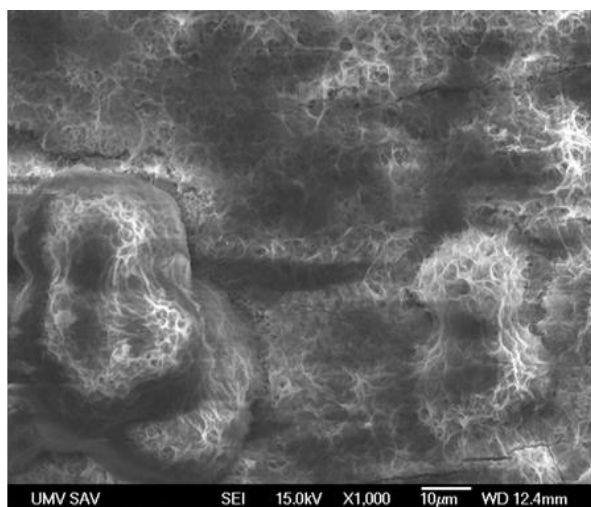
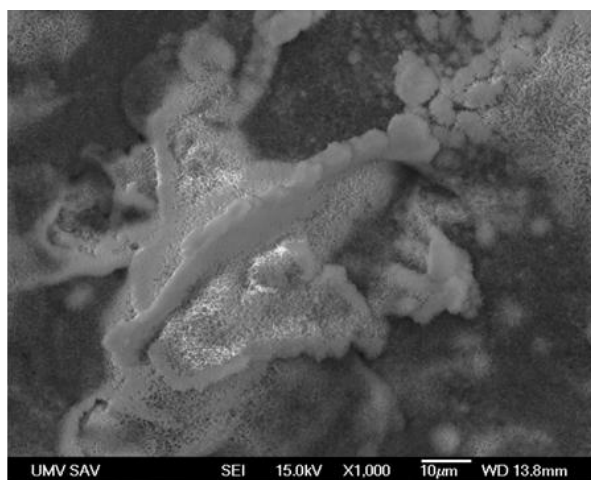
Fig.3 alfa HDG during exposure in 3%NaCl with final corrosion mass loss of zinc $46,61\text{g.m}^{-2}$ **Fig.4** gamma HDG during exposure in 3%NaCl with final corrosion mass loss of zinc $Zn = 7,48\text{g.m}^{-2}$ **Fig.5** GI HDG sample during exposure in 3%NaCl with final corrosion mass loss of zinc $Zn = 30,26\text{g.m}^{-2}$ 

Fig.6 alfa HDG after 30-days of exposure in 3% NaCl**Fig.7** alfa HDG after 30-days of exposure in ECO salt solution**Fig.8** alfa HDG after 30-days of exposure in condensation chamber

The protection of zinc coatings on HDG samples exposed in 3% NaCl were completely lost, surface was locally deteriorated and the rest of zinc coatings were separated from steel substrate (Fig.6). This phenomenon lead to effect that application of non-destructive technique of corrosion monitoring based on electrochemical noise was not able to detect any R_N value. The reason is that technique is able to detect values higher than $1000 \Omega \cdot \text{cm}^2$ and was below sensitivity of ENA NOCS setup.

Zinc coating on HDG steel exposed to the ecological salt solution were completely covered by corrosion products with net structure and passivation character. The proof of this fact were

supported by gravimetry, samples do not have any corrosion mass losses after 30 days of exposure to eco salt.

The same effect was observed on HDG steel samples exposed in condensation chamber, surface were covered by corrosion products with "needle" structure and passivation character mainly consisted of ZnO, ZnCO₃ and common hydrozincites.

Corrosion monitoring technique with support of gravimetrical changes and scanning microscopy has shown that during exposition of alfa HDG samples, these start to passivate in condensation chamber after 15 days and in ecological salt solution after 30 days. For alfa HDGsteels in 3% NaCl only active state were detected.

4 Conclusions

The paper demonstrates ability of electrochemical noise method in no contact to the substrate arrangement to be used as corrosion monitoring technique for fast detection of active/passive state of zinc coatings. The obtained R_N values for active surface lie in few tens of $\Omega \cdot \text{cm}^2$ range, these of low activity, resp. passivity in hundreds of $\text{k}\Omega \cdot \text{cm}^2$. It was also shown that ecological salt solution is much lower aggressive than 3% NaCl according to the norm EN ISO 11130:2011 for all alfa HDG steels. This results were supported by gravimetrical analysis where mass losses do not exceed $1.5 \mu\text{g} \cdot \text{m}^2$. The passivity and protection character of zinc corrosion products after exposure in ecological salt solution and condensation chamber was proven also by scanning electron microscopy. The values of R_N were not obtained for deteriorated zinc coatings after 30 days of exposition in 3% NaCl due to the pre-corroded zinc surface which was also visually observed. It was also shown that during exposition of alfa HDG samples in condensation chamber after 15 days and in ecological salt solution after 30 days initiation of passivation got started. For alfa HDG steels in 3% NaCl only active corrosion was observed.

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