

Atmospheric degradation of zinc-nickel alloy electrodeposited coatings

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Summary

The electrodeposited zinc coating with additional passivation had been widely used for corrosion protection of many parts and products. This type of surface treatment is now replaced by many other systems – one of them is electrodeposited zinc coating alloyed by nickel. This coating has high corrosion resistance in accelerated corrosion salt spray test. These two types of coating were exposed in atmospheric conditions for 5 years. The different mechanisms of corrosion attack are evaluated.

Key words: Zn–Ni alloy coating, corrosion behaviour, field atmospheric test, corrosion mechanisms, localized type of corrosion, pitting

1 Introduction

Corrosion protection of ferrous substrates by means of sacrificial zinc-based coatings is well established in the surface coatings industry. As results of EU directives the surface treatment of substrate steel by electrodeposited zinc coating with additional passivation by hexavalent chromium was in many cases replaced by application of Zn-Ni alloy electrodeposited coating. The zinc-nickel alloy coating has higher corrosion resistance compared to electrodeposited zinc. For this coating the cracking structure is characteristic.

The corrosion mechanism of Zn–Ni alloy coating differs from traditional zinc coating. Several corrosion mechanisms for electrodeposited zinc-nickel coating have been suggested [1] - 5]. The Zn-Ni coatings have a tendency to quickly production of white corrosion which is different to zinc corrosion products. In the first stage of corrosion attack of Zn–Ni alloy coating in all basic corrosion conditions the effect of „white-grey veil“ occurs. This very thin layer is different from the typical white corrosion products of zinc coating (Fig. 1).

Other specific corrosion phenomenon is the localized corrosion of substrate steel without significant corrosion of Zn-Ni coating but with possible pitting corrosion of this coating. The reasons of the pitting corrosion of Zn-Ni coating are probably different in respect to exposure conditions – penetration of corrosion stimulators through cracks and/or de-alloying of Zn-Ni coating. The first manifestation of corrosion of substrate steel had been found after 20 cycles (480 hrs) of humidity test and after 3 months of atmospheric test at locality without salinity deposition (Fig. 2). The diameter of pits was in range from 0.1 to ca 5 mm.



Figure 1: White-grey veil formed in different corrosion conditions



Figure 2: The corrosion of substrate steel after 3 months exposure on atmospheric test site

2 Tested samples and exposure conditions

The atmospheric test was performed on the samples of the common components of automobile industry with Zn-Ni alloy electrodeposited coating of ca 12% Ni and thickness 8 μm . The subsequent surface treatments were different – chromate with Cr^{III} (A) or trivalent chromate + sealing (A/T2) – see Table 1.

The samples had been exposed on the rack on the atmospheric test site Kopisty, the Czech Republic. The atmospheric exposure started in 2005 and was finished in 2011 after 6 years with periodical evaluation and samples' withdrawal. The basic environmental data for this period are given in Table 2. Corrosivity of test site atmospheres were estimated according to ISO EN 9223 in 2006 and 2009 and the corrosivity category for zinc was C3 – the salinity of locality is on background ($\leq 3 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$).

Table 1: Samples' description

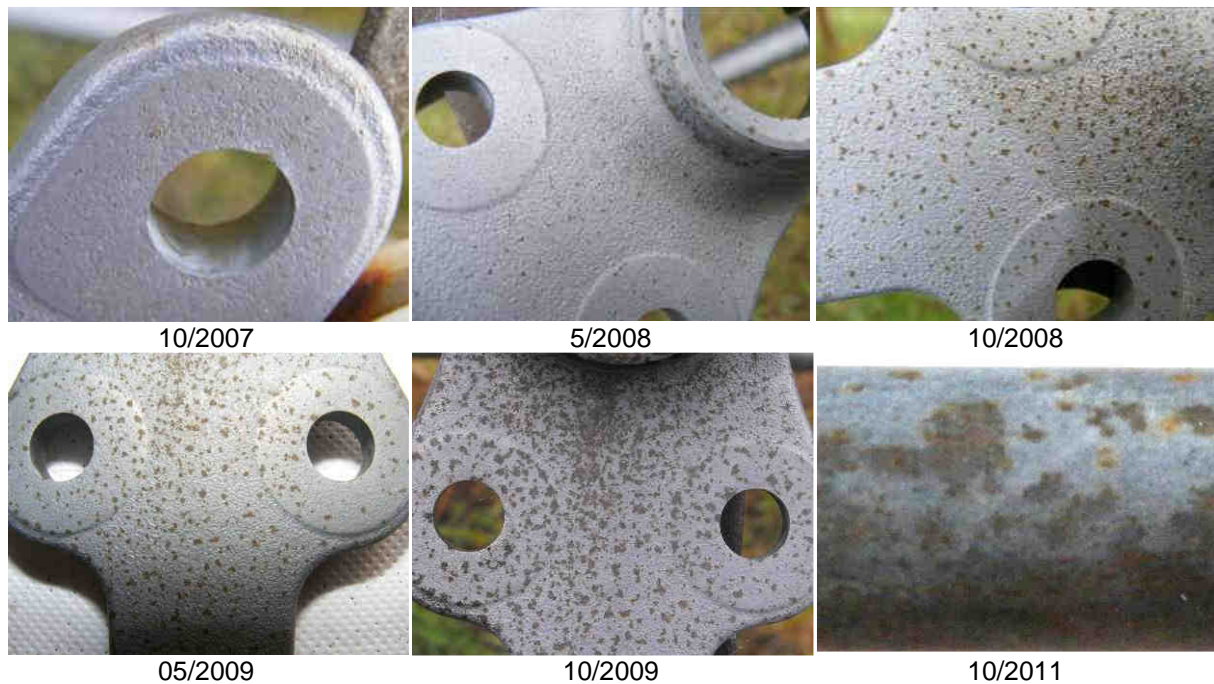
sample	part	surface treatment
1	pin	Fe/ZnNi (12)8/A
2	head	Fe/ZnNi (12)8/A
3	rod	Fe/ZnNi (12)A/T2
4	ball stud	Fe/ZnNi (12)A/T2
5	ring	Fe/ZnNi(12)8/A

Table 2: Yearly average values of environmental parameters

year	T [°C]	RH [%]	rain* [mm]	SO ₂ [µg.m ⁻³]	NO _x [µg.m ⁻³]	pH of precipitation
2005	8,9	77	514	12,6	23,9	6,0
2006	8,9	76	406	18,6	25,7	5,6
2007	10,0	77	624	15,6	27,3	5,3
2008	9,6	79	506	10,0	24,0	6,1
2009	9,3	80	556	14,1	23,0	6,1
2010	8,1	79	647	17,2	27,4	4,9
2011	9,6	80	480	16,3	33,9	6,0
average yearly sum	9,2	78	533	14,9	26,5	5,7

3 Corrosion attack evaluation

The atmospheric corrosion had been evaluated on the automotive compounds with Zn-Ni coating and various types of additional surface treatments (see Table 1) – Fig. 3. The detailed study had been performed for samples exposed for 1 and 5 years.

**Figure 3:** Progress of corrosion attack of Zn-Ni coating exposed at test sites Kopisty

After one year exposures at atmospheric test site the small stains of corrosion products of substrate steel had been evident (Fig. 4). The details of corrosion attack of Zn-Ni coating layer are evident from cross section of samples. The corrosion attack of substrate steel surface under the layer of Zn-Ni coating had been found and the presence of sulphur as a dominant corrosion stimulator was proved by mapping by scanning electron microscope (Fig. 5c). The corrosion attack of substrate steel is manifested in the cracks of Zn-Ni coating.

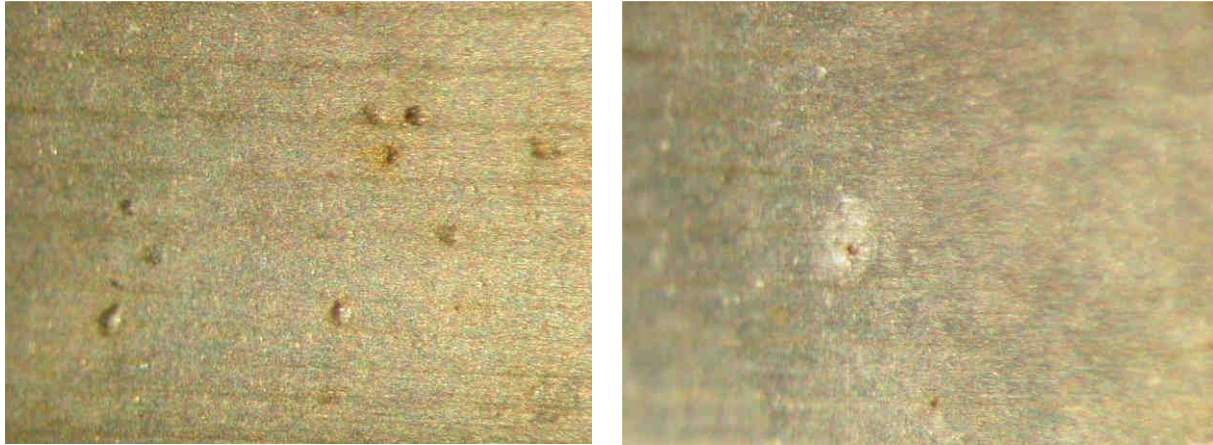


Figure 4: The details of corroded Zn-Ni coating exposed 1 year at test sites Kopisty

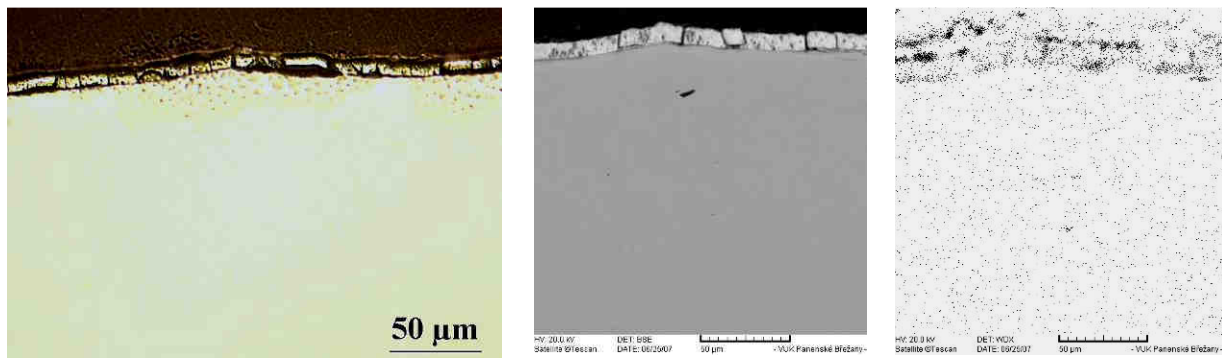


Figure 5: The cross section of corroded Zn-Ni coating exposed 1 year at test sites Kopisty in light and scanning electron microscopy and the distribution of sulphur

The detail of corroded surface after 5 years of exposure is given on Figs. 6 and 7. The cross section shows the blister of corrosion product of substrate steel which caused the lost of adhesion of electrodeposited alloy Zn-Ni coating. The distribution of elements on the exposed surface shows the lower concentration of nickel in cracks and increased concentration of sulphur as dominant corrosion stimulator in the corrosion stain of substrate steel on the coating surface.

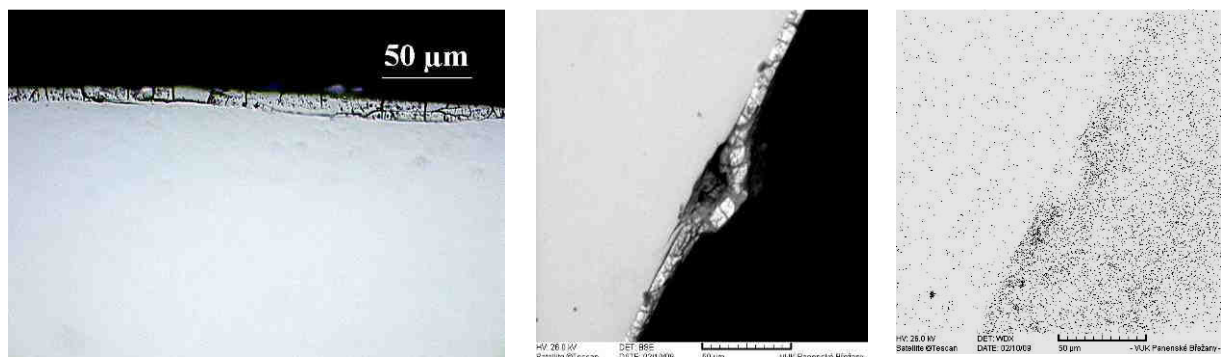


Figure 6: The cross section of corroded Zn-Ni coating exposed 5 year at test sites Kopisty in light and scanning electron microscopy and the distribution of sulphur

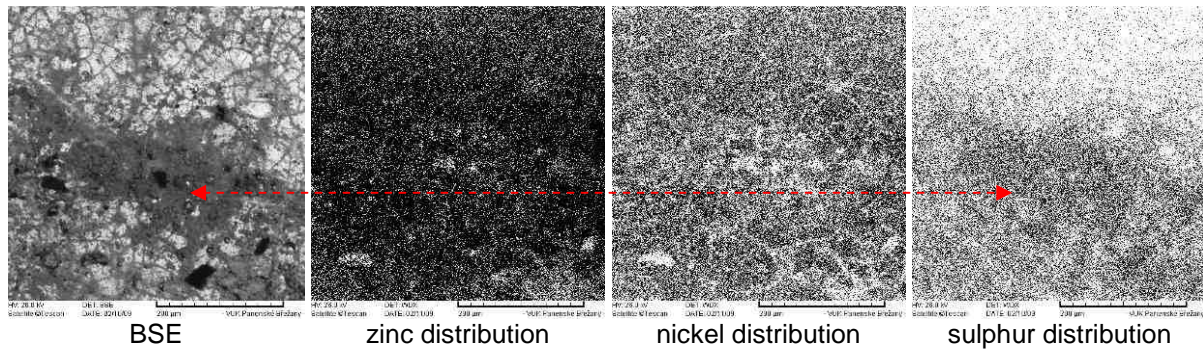


Figure 7: The surface of corroded Zn-Ni coating exposed for 5 year at test sites Kopisty in scanning electron microscopy and the distribution of Zn, Ni and S

With the time of exposure the corrosion attack of Zn-Ni coating in the form of stains of corrosion product of substrate steel increased without any significant occurrence of corrosion product of zinc (Fig. 3). The corrosion attack formed as pits with the depth ca 40 µm after relative short exposure and this depth left the steady during the following exposure only the diameter of pits increased and pits jointed together (Fig. 8).

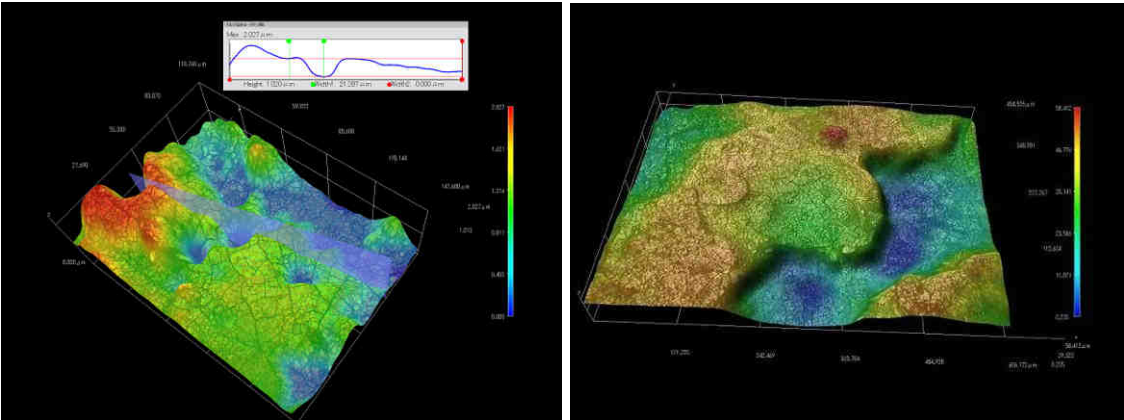


Figure 8: The profile of corroded Zn-Ni coating exposed 2 years (left) and 5 years (right) at test site Kopisty evaluated by Hirox microscope

Conclusion

The results of dominantly used accelerated salt spray laboratory test have only limited relation to real service life of parts with Zn-Ni coatings. In real automotive environment the both hypothetic mechanism of Zn-Ni coating localised pitting corrosion will occur depending on area of application of parts in automotive body, mainly from point of view of de-icing salts effects. This specific corrosion behaviour of Zn-Ni coating should be consider for evaluation of suitability of this surface treatment and should perform the accelerated corrosion tests with various regimes.

During last 2 – 3 years the requirements of testing this coating into accelerated laboratory test - sulphur dioxide test with general condensation of moisture (Figs. 9 and 10). The corrosion products were indentified as dominant $ZnSO_3 \cdot 2.5H_2O$ and traces of $Ni(SO_3)_2 \cdot 6H_2O$ after 1 cycle of this test. The resistance of the coating in this

test is very low due to cracks in coating structure. The most reliable results give the field test of this coating.



Figure 9: Component with Zn-Ni alloy coating corrosion attack after 600 hrs of NSS test (left) and 5 cycles in test with SO₂ (2 L dosage) (right)

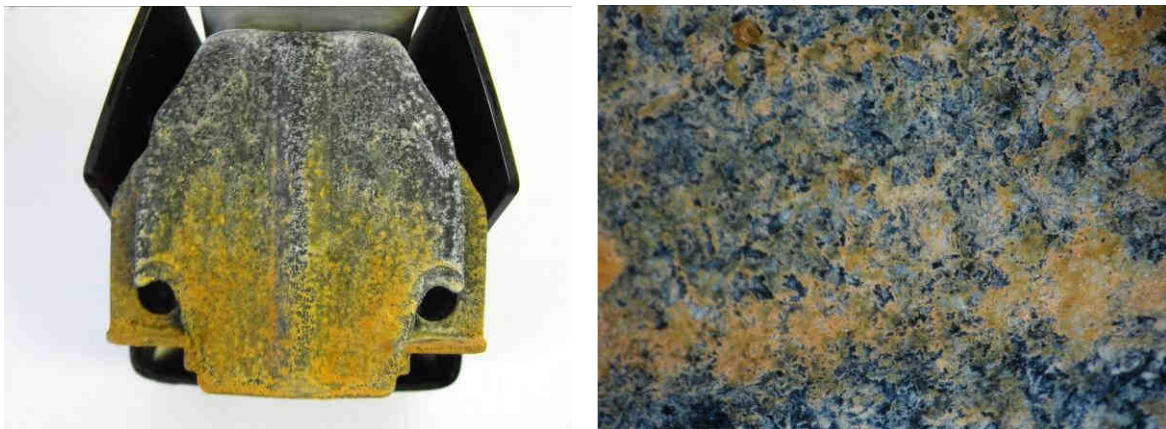


Figure 10: Component with Zn-Ni alloy coating corrosion attack after 3 cycles in test with SO₂ (2 L dosage)

Zinc-nickel coating has high corrosion resistance and has been widely applied for various usages. The widely used laboratory accelerated test for testing of Zn-Ni corrosion resistance is the neutral salt spray test. The Zn-Ni coatings have a tendency to produce quickly a white corrosion – grey veil – at all performed tests. Other specific corrosion phenomenon is the localized corrosion of substrate steel. The localised pitting corrosion of ZnNi coatings occurred at all performed test in very wide range of exposure periods. The reasons of the pitting corrosion of Zn-Ni coating are probably different in respect to exposure conditions:

- in accelerated corrosion test by neutral salt spray or cyclic test included this exposure together with thermal stress the corrosion mass loss of zinc is quick and formation of a Ni-enriched surface layer. The forming of coating with higher

content of nickel and higher electrochemical potential is supposed as a reason of pitting corrosion.

- in condition of less intensive corrosion stress is probably the reason of pitting corrosion of Zn-Ni coating the penetration of environment through cracks to substrate steel. This type of corrosion attack does not occur on Zn-Ni coatings with black chromate and sealing.

In real automotive environment the both hypothetical mechanism of Zn-Ni coating localised pitting corrosion will occur depending on area of application of parts in automotive body, mainly from point of view of de-icing salts effects. This specific corrosion behaviour of Zn-Ni coating should be consider for evaluation of suitability of this surface treatment and should perform the accelerated corrosion tests with various regimes. Automotive producers should define acceptable range of pitting corrosion - the intensity and size of pits after exposure at accelerated corrosion tests.

To improve the protective properties of Zn-Ni coating the various study had been done [6, 7] but if the cracking structure would not be sealed the same corrosion behaviour can be expected.

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