Corrosion properties of systems based on ZrO$_2$ sol-gel films on Zn-Ni and Zn-Co alloys

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The presented investigations demonstrate the corrosion behavior and protective ability of two composite systems obtained on low-carbon steel in model corrosive medium of 5% NaCl solution. These systems consist of Zn-Co (3 wt.%) or Zn-Ni (10 wt.%) alloy coatings as an under-layer and very thin ZrO$_2$ sol-gel film as a top-layer. The surface morphology of the samples was studied with scanning electron microscopy (SEM). Their corrosion resistance was investigated by application of potentiodynamic polarization (PDP) curves, polarization resistance measurements (Rp) for a definite period of time (10 days) and electrochemical impedance spectroscopy (EIS). The results obtained were compared with the corrosion characteristics of an ordinary zinc coating with the same thickness. The experimental data present the positive influence of the newly developed composite systems for the enhanced protective properties of low-carbon steel in the test aggressive chloride-containing environment.

Keywords: corrosion, zinc, Zn-based alloys, ZrO$_2$ sol-gel film

INTRODUCTION

It is well known that steels are widely applied traditional materials in the transport industry, as well as for buildings, bridges, railway facilities, etc. However, their implementation often involves significant financial costs combined with the need for increased corrosion resistance. In that sense the application of low-carbon steels gives one more opportunity due to their lower cost combined with good mechanical and other parameters. Depending on the surrounding conditions these materials often demonstrate good corrosion characteristics especially if an additional protective surface film (metallic, sol-gel oxide, conversion, etc.) is available. One possible and economically viable approach for better protection of the low-carbon steel is the galvanizing [1-3].

The practical role of zinc is generally as a sacrificial coating since this metal is destroyed firstly during the corrosion processes, thus forming a protective layer of corrosion products with a low product of solubility value. It is observed that this layer can slow-down the corrosion rate depending on the aggressive medium. As well known, the protective characteristics of the zinc can be significantly enhanced by its alloying with Ni, Co, Mn, etc. [4-7].

In recent years, many researchers investigated the sol-gel coating types like TiO$_2$, ZrO$_2$, etc. which attracted considerable attention due to their ease of manufacturing, low cost, better mechanical stability and corrosion resistance. They also demonstrate good mechanical strength, hardness, wear resistance and chemical inertness. The deposition procedures are object of intensive research worldwide. In addition, multilayer systems provide in general better protective ability compared to single-layer coatings [8-11]. To the best of our knowledge the information on the deposition of such films on galvanized low-carbon steel and on Zn-based alloys, respectively, is rather scarce.

The aims of the present investigation are to obtain composite systems consisting of zinc-based alloy coatings - Zn-Co (3 wt.%) or Zn-Ni (10 wt.%) as under-layers and ZrO$_2$ sol-gel amorphous top film, to characterize their corrosion behavior in chloride-containing test medium and to compare the obtained experimental data with the corrosion properties of ordinary electrodeposited zinc.

MATERIALS AND METHODS

Sample types

Low-carbon steel plates with sizes 30 × 10 × 1 mm and composition (wt.%): C - 0.05–0.12; S ≤ 0.04; P ≤ 0.35; Mn - 0.25–0.5; Cr ≤ 0.1; Si ≤ 0.03; Ni ≤ 0.3; Cu ≤ 0.3; As ≤ 0.08; Fe - balance were used

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as substrates. Following systems were obtained on the latter:

- System 1: Zn-Ni (10 wt.%) – under-layer / ZrO$_2$ – top-layer;

- System 2: Zn-Co (3 wt.%) – under-layer / ZrO$_2$ – top-layer.

The zinc-based alloy coatings (as well as the ordinary zinc) were electrodeposited with practically equal thickness of about 11-12 μm, followed by deposition of ZrO$_2$ sol-gel layer according to the procedures described below.

System 1 – Zn-Co (3 wt.%) alloy coatings were obtained from an electrolyte containing 100 g/L ZnSO$_4$.7H$_2$O, 120 g/L CoSO$_4$.7H$_2$O, 30 g/L NH$_4$Cl and 25 g/L H$_3$BO$_3$ at pH 3.0–4.0, soluble zinc anodes and additives ZC-1 (wetting agent - 20 ml/L) and ZC-2 (brightener - 2 ml/L) [5]. Electrodeposition conditions: cathodic current density 2 A/dm^2, ambient temperature ~ 25 °C, no stirring, soluble zinc anodes, time – 20 minutes.

System 2 – Zn-Ni (10 wt.%) alloy coatings were obtained in a thermostated electrolytic cell with circulation from an electrolyte with a composition: 100 g/L NiSO$_4$.7H$_2$O, 100 g/L NiCl$_2$.6H$_2$O, 30 g/L ZnCl$_2$, 10 g/L β-alanine at pH ~ 4; cathodic current density 2 A/dm^2, temperature 40 °C, non-soluble Ti-Pt networks as anodes [6].

Ordinary zinc coating was electrodeposited from an electrolyte with composition 150 g/L ZnSO$_4$.7H$_2$O, 30 g/L NH$_4$Cl and 30 g/L H$_3$BO$_3$, pH 4.5-5.0, cathodic current density 2A/dm^2, soluble zinc anodes, 2 additives: wetting agent (AZ1), brightener (AZ2) [5].

ZrO$_2$ sol-gel layers were obtained from zirconium butoxide Zr(OC$_4$H$_9$)$_4$ diluted with isopropanol and some amounts of acetyl acetone and acetic acid (complexing agents). Next step was to add nitric acid and polyethylene glycol (PEG400). The final solution was diluted up to 0.2M and stirred for 2 h until appearance of yellowish-transparent color. Low-carbon steel samples, previously galvanized with Zn-Co (3 wt.%) or Zn-Ni (10 wt.%) alloy were immersed into the zirconium precursor solution and after withdrawing (rate of 30 mm/min) were dried at room temperature and subsequently at 100°C for 30 min. The deposition and drying of ZrO$_2$ coating were repeated 3 times [12, 13]. The final treatment was carried out at 380°C for 1 h.

SEM studies

The surface morphology of the investigated systems was studied with a scanning electron microscope INCA Energy 350 unit.

Potentiodynamic investigations

Potentiodynamic polarization (PDP) curves were obtained in a three-electrode glass cell with a volume of 300 mL. These measurements were performed in the range of ~ −1.2 to ~ +0.3 V at a scan rate of 1 mV/s. Reference electrode was saturated calomel electrode (SCE) while a platinum wire was the counter. The initial potential was chosen at ~150 mV cathodically to the corrosion potential and the scan was stopped at the moment of the fully disappearing of the protective system from the sample surface. VersaStat 4 PAR device was applied to realize these investigations [12, 13].

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were also realized with the VersaStat 4 PAR device in the same electrochemical cell. The measurements were carried out in the frequency range of 100 kHz to 10 mHz (potentiostatic mode) by superimposing an AC voltage of 10 mV after establishing a constant potential value.

Polarization resistance

This method was applied for checking the protective ability of the coatings toward the substrate as it is well known that the Rp value is inversely proportional to the corrosion current density according to the Stern-Geary equation [14]. The investigations were carried out with the "Corrovit" device specially designed for this type of measurements.

Corrosive medium

Electrochemical corrosion tests were performed in a 5% NaCl solution as model corrosion medium at pH 6.7 and ambient temperature.

Reproducibility

The results from the investigations were an average of 5 samples per type and per stage, i.e. for each measurement 5 replicates were conditioned for the measurements.

RESULTS

SEM studies

The surface morphology of the samples is demonstrated in Figure 1. The surface of the ordinary zinc is smooth and even, while this of System 1 is covered with some crack zones of different shape, width and depth. They are similar and somewhat reminiscent of the surface of previously well-known hexavalent chromium-based conversion films, the latter being subsequently banned for environmental reasons [15-18].

Zn-Co(3wt.%)/ZrO$_2$ Zn-Ni(10wt.%)/ZrO$_2$

Zn
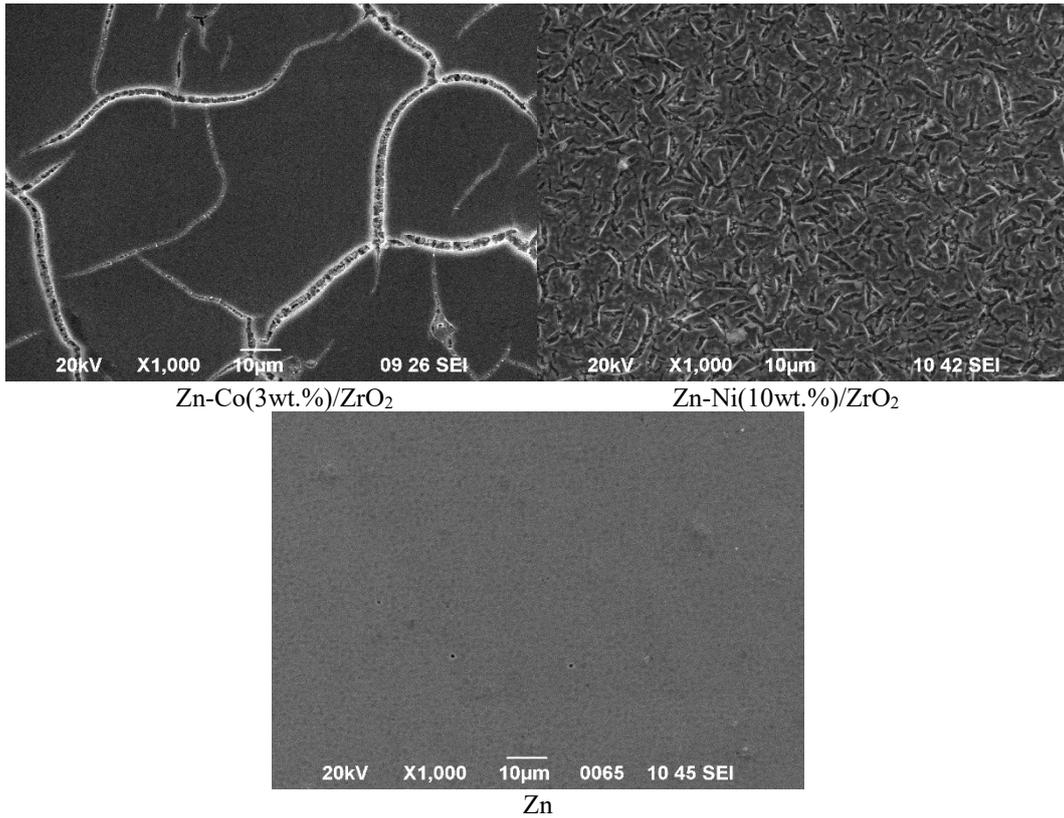
Figure 1. SEM images of the investigated samples

The surface of System 2 also differs compared to both other samples - it is somewhat grooved and to a certain degree uneven. These results clearly show that the nature of the under-layer is of significant importance for the final surface morphology of the obtained systems. A possible explanation for these results could be sought in the differences in the thermal expansion coefficients of zinc (from one side) compared to Fe, Co and Ni since these parameters strongly differ, as well as in some physical and chemical parameters of the surface (morphology, hydrophobicity, etc).

Potentiodynamic investigations
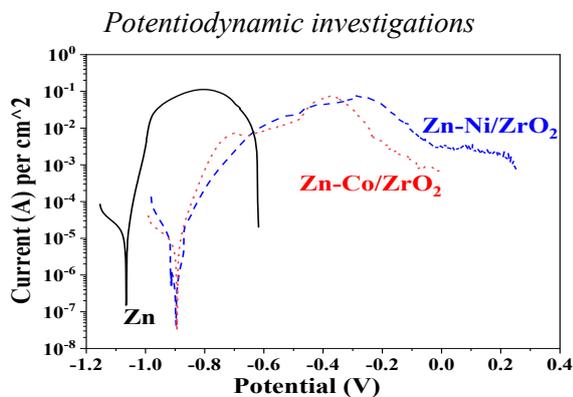
Figure 2. PD curves of the investigated samples in 5% NaCl model medium

The PDP curves of the investigated systems can be observed in Figure 2. It is evident that the ordinary zinc coating shows the shortest curve in the anodic zone which means that it lasts shorter time at external anodic polarization compared to both other samples. The curves of System 1 and System 2 are in general close in their course. Some differences appear for System 1 in the anodic branch – zones with higher and lower current density values especially in the potential interval of -0.7 – 0.35 V. The reason for this observation could be the availability of some cracks on the surface which could cause tearing off some scales during the anodic polarization leading to deeper penetration of the chloride ions. Another important parameter is the length of the anodic branch of the curves – it is well visible that System 2 shows a longer curve (with about 200 mV) which is a sign for higher corrosion resistance in that medium at these conditions.

Some important parameters of the PD curves – corrosion potential E_{corr}; corrosion current density I_{corr}; maximal anodic current density I_{max} - are summarized in Table 1.

Table 1. Electrochemical parameters of the PDP curves from Figure 2

Sample	E_{corr}, mV	I_{corr}, A.cm^{-2}	I_{max}, A.cm^{-2}
Zn	-1.065	$1.8.10^{-5}$	0.121
Zn-Co/ZrO$_2$	-0.895	$7.7.10^{-6}$	0.086
Zn-Ni/ZrO$_2$	-0.895	$5.3.10^{-6}$	0.084

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Electrochemical impedance spectroscopy

The results from the EIS measurements are demonstrated in Figure 3. It can be observed that they are generally in quantitative correlation with the PDP curves. One of the most important parameters that briefly gives a reliable information concerning the protective characteristics of the investigated objects is the Z_{re} value measured on the X axe. This parameter is associated with the polarization resistance, the latter being inversely proportional to the corrosion current. It is obvious that the ordinary zinc has the lowest value – about 117 ohms. Both other investigated samples with a surface sol-gel layer demonstrate values of 158 ohms for System 1 and 162 ohms for System 2. These values are very close which could be partially explained with the nature of the film (from one side) and with short immersion times (up to receiving of a stabilized open circuit potential OCP - value).
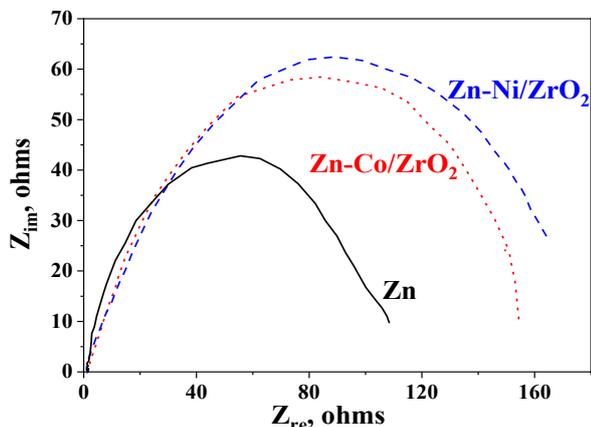
Figure 3. EIS spectra of the investigated samples in 5% NaCl model medium

Polarization resistance

The experimental results from the polarization resistance measurements for a time period of 10 days are demonstrated in Figure 4. It can be summarized that the Rp values of the ordinary zinc remain very close during the whole period being the lowest compared to both systems. Contrary to this System 1 shows gradually increasing values with a peak on the 4th day and a high Rp value of about 9000 ohms.cm² at the end of the test. The other investigated system – S2 – presents the highest Rp at the 10th day although very close to S1. These results clearly confirm the positive influence of the applied thin ZrO₂ sol-gel layer on the protective characteristics of the newly developed systems in that medium.
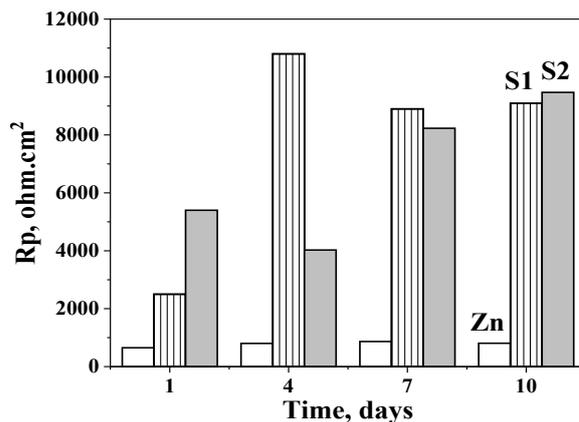
Figure 4. Polarization resistance (Rp) of the investigated samples in 5% NaCl model medium (S1 – System 1; S2 – System 2)

CONCLUSIONS

The obtained composite systems based on two types of selected zinc alloys coated with a top ZrO₂ sol-gel layer showed improved protective characteristics toward the low-carbon steel substrate compared to the ordinary zinc in a model medium with chloride ions as corrosion activators. The reason for this statement is the experimental data obtained by application of the selected methods. The polarization resistance of both systems at the end of the test period is about 10 times higher compared to the ordinary zinc. The other methods lead to less similar results which could be expected especially if taken into account that they are realized at much shorter test time and different conditions – for example, the potentiodynamic curves are realized at external polarization. Generally, the EIS spectra and SEM studies confirm the obtained experimental results. The latter can serve as a basis for further improvement of the protective characteristics of these systems, as well as to development of other protective types in order to prolong their service life.

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