Electrochemical Evaluation of Corrosion Resistance of Trivalent Chromate Conversion Coatings with Different Organic Additives

Thanyalux WANOTAYAN, Yuttanant BOONYONGMANEERAT, Joongjai PANPRANOT, Eiji TADA and Atsushi NISHIKATA

1) Nanoscience and Technology Interdisciplinary Program, Graduate School, Chulalongkorn University, Pathumwan, Bangkok, 10330 Thailand. 2) Surface Coatings Technology for Metals and Materials Research Unit, Metallurgy and Materials Science Research Institute, Chulalongkorn University, Pathumwan, Bangkok, 10330 Thailand. 3) Department of Chemical Engineering, Engineering Faculty, Chulalongkorn University, Pathumwan, Bangkok, 10330 Thailand. 4) Department of Chemistry and Material Science, Tokyo Institute of Technology, Meguro-ku, Tokyo, 152-8552 Japan.

(Received on January 19, 2018; accepted on April 12, 2018)

The corrosion resistance of electrogalvanized steels with trivalent chromate conversion coatings is investigated electrochemically to analyze the effect of organic additives on the corrosion resistance under wet-dry cyclic conditions. Three sets of polyamine additives, namely (i) imidazole and epihaloxydrin, (ii) polyquaternary amine salt, and (iii) polyethyleneimine, are examined and compared. Electrochemical impedance spectroscopy and anodic stripping were employed to evaluate the corrosion resistance. Crystal-structure and compositional analyses were also applied to demonstrate the role of organic additives in controlling the structure of the zinc layer and the formation of the trivalent chromate conversion film.

KEY WORDS: electrogalvanized steel; trivalent chromate; organic additives; atmospheric corrosion; EIS; anodic stripping.

1. Introduction

Electrogalvanized chromate steels are widely used for corrosion protection in various applications, including automotive, construction, and electrical. To apply the coating, a steel substrate is submerged and electrochemically plated in a zinc bath and subsequently dipped in a chromium-based passivation solution. The alkaline non-cyanide zinc plating solution and Cr3+-based passivation solution are environmentally-friendly chemicals that are available for these processes. The key chemicals in the zinc plating solution include organic additives, such as organic polyamine compounds, which affect the uniformity, leveling, and brightness of the zinc coatings.

Several studies have reported the effect of organic additives on the development of the microscopic features and structures of galvanized deposits, and subsequently on the plating characteristics and coating appearances. Since the corrosion resistance of zinc coatings is known to relate their microstructures, it could be anticipated that organic additives also play an important role in controlling the corrosion properties of galvanized deposits. Nevertheless, studies that aim to systematically verify and explain such relationships are currently limited.

Electrochemical techniques are very powerful in evaluating the corrosion resistance of galvanized steels. Electrochemical impedance spectroscopy (EIS) is especially suitable for monitoring the degradation of galvanized steels exposed to accelerated corrosion tests and natural environments because it is a non-destructive method. The corrosion rate can be estimated from the charge transfer resistance that appears in the lower frequency region. Meanwhile, a galvanostatic stripping method is a very convenient but destructive technique for evaluating the thickness of zinc coatings. In this work, by using these electrochemical techniques, we investigate and analyze the effects of organic additives on the corrosion behavior of alkaline non-cyanide zinc-based electrogalvanized coatings and their corresponding trivalent chromate conversion coatings. Three common organic polyamine additives, namely imidazole and epihaloxydrin, polyquaternary amine salt, and polyethyleneimine, are chosen as representative additives in the study. The corrosion resistance is particularly examined under wet-dry cyclic conditions in a saline environment, and analyzed using EIS. In addition, the thickness reduction of the zinc coatings due to corrosion is evaluated by an anodic stripping method. The employed cyclic test conditions have been identified as an accelerated test protocol that closely simulates a typical unsheltered atmospheric saline environment. The understanding gained from this study provides an insight into how chemical additives play a role in controlling the corrosion behaviors of industrially-important galvanized coatings.
2. Experimental

2.1. Sample Preparation

Three sets of electrogalvanized deposits were prepared on low-carbon steel substrates (5 × 7 × 0.1 cm²) with the following composition in %: C, 0.044; Si, 0.0065; Mn, 0.248; P, 0.018; Cr, 0.027; Ni, 0.014; Al, 0.014; Cu, 0.0082; and Fe, 99.55. The substrates were pretreated by soaking in 30% NaOH at 323 K for 1.8 ks, electrocleaning in 5% NaOH at 298 K and 5 V for 30 s, and dipping in 5% HCl at 298 K for 10 s. The electrodeposition was performed at 298 K in alkaline non-cyanide zincate baths (Na₂Zn(OH)₄), containing 10 g/L of Zn and 120 g/L of NaOH and 1 mL/L of selected additives, including imidazole and epiphosphorydin (Lugalvan IZE, BASF, Germany) for bath #1, a polyquaternary amine salt (Lugalvan P, BASF, Germany) for bath #2, and polyethyleneimine (Lugalvan G35, BASF, Germany) for bath #3. The resulting specimens from the three baths are designated EZ1, EZ2, and EZ3, respectively. For each, a direct current of 2 A/dm² was applied for 1.8 ks to the plating cell containing carbon steel as an anode. After deposition, a separate set of samples from each bath was passivated with a commercial trivalent chromium-based solution (OKUNO Chemical Industries). The trivalent chromate conversion process consisted of surface activation in 1% HNO₃ for 10 s, dipping in a Cr³⁺-based solution at 303 K with a controlled pH of 2.2 for 45 s, applying a top coat, and oven-drying at 353 K for 1.8 ks. Based on the numbers of their zinc baths, the samples are named EZP1, EZP2, and EZP3, respectively.

2.2. Corrosion Test

Seven samples from each group were used for the corrosion test. The edges of the samples were covered with tape, leaving an exposed area of 3.14 cm². A NaCl solution was deposited on the surface of the sample at a concentration of 5 g/m². The samples were then placed in the chamber and subjected to wet-dry cycles comprising 2 h drying and three recurring measurements were done for each time was fixed to one min to collect sufficient statistic count. Every week, these samples were cleaned with water, and fresh NaCl solution was applied to the surface before returning to the chamber. An optical microscope (OM) was used to observe the corrosion products on the sample surface, and the remaining thickness of the zinc coating was determined by an anodic stripping method. Additionally, one sample from each group in the corrosion experiment was reserved for weekly EIS measurement for impedance monitoring.

2.3. EIS Measurement

All electrochemical analyses were conducted in a three-electrode cell with silver/silver chloride (Ag/AgCl, sat. KCl, SSE) as a reference electrode, platinum wire as a counter electrode, and a sample as a working electrode. The samples were immersed in 10 mM NaCl solution at room temperature. Using an electrochemical measurement system (Bio-Logic VSP), EIS measurements were performed at open-circuit potential with a 10 mV amplitude, and the impedance spectra were recorded in the frequency range 1 kHz–1 mHz.

2.4. Anodic Stripping Measurement

To determine the corrosion rates of the zinc coatings, the remaining zinc coating thickness of the galvanized samples exposed to the wet-dry cycles was measured by the anodic stripping method. During anodic stripping, the remaining zinc coating was dissolved by anodic polarization at a constant current of \( i_s = 500 \mu A \text{ cm}^{-2} \) for the first week, and \( i_s = 200 \mu A \text{ cm}^{-2} \) for the remaining week. Figure 1 shows a typical stripping curve of EZ1 after one week’s exposure to the corrosion test. A rapid potential shift in the positive direction is observed at \( t_s \) (about 27.5 ks), indicating that all the zinc coating has dissolved. The thickness of the zinc coating \( d(\mu m) \) can be estimated using Eq. (1),

\[
\frac{d}{\mu m} = \frac{i_s \tau_s W_{Zn} \times 10,000}{2FD_{Zn}} \tag{1}
\]

where \( i_s \) is the current density (2 × 10⁻⁴ A cm⁻²), \( W_{Zn} \) and \( D_{Zn} \) are the molar mass (65.4 g mol⁻¹) and density (7.14 g cm⁻³) of zinc, respectively, and \( F \) is the Faraday constant (C mol⁻¹). From the stripping curve in Fig. 1, the remaining thickness of the zinc coating after one week’s exposure is estimated to be about 6.5 μm.

2.5. Sample Characterization

Optical and scanning electron microscopy (OM and SEM) were used to analyze the surface appearance and cross-sectional structure of the coatings, respectively. To characterize the chemical and phase compositions, X-ray fluorescence (XRF) and X-ray diffraction (XRD) were applied to the outer surface of the specimen. The XRF spectrometry is equipped with an X-ray tube, a silicon drift detector with 140 eV resolution (Mn Kα), and a large measurement chamber that can be evacuated. The coating surface was bombarded with X-rays, and elemental analysis of the coating layers was performed. The XRF measuring time was fixed to one min to collect sufficient statistic counting and three recurring measurements were done for each analysis point. The ratio of Cr/Zn was calculated using the average value from five analysis points throughout the surface. XRF was also used to determine the initial thickness of the coating layers.

Fig. 1. A typical anodic stripping curve at 500 μA cm⁻² for EZ1 after one-week exposure to the corrosion test.
3. Results and Discussion

3.1. Sample Characteristics

Specimens from all groups were successfully fabricated with good surface uniformity and no visually observable defects. Figure 2 shows a representative cross-sectional microstructure of a columnar-grained galvanized deposit covered with a relatively thin trivalent chromium conversion layer (EZP2). The thicknesses of the zinc and trivalent chromium coatings are approximately 11 and 0.5 μm, respectively.

Before exposure to the wet-dry cycles, the initial thicknesses of all the zinc coatings employed in the corrosion test were measured by XRF and are shown in Table 1. The thicknesses varied slightly within groups, especially EZP1. Meanwhile, all zinc coatings were electroplated using the same quantity of electricity (2 A/dm², 1.8 ks), but their thicknesses varied in the order EZ1 < EZ2 < EZ3. This is attributed to differences in the adsorption capacity of their organic additives. The thickness also appeared to be changed after chromate treatment.

While zinc is the key component in the galvanized layer, the passivation layer comprises chromium and zinc in the form of oxides and hydroxides. XRF analysis identified that, among different EZP groups, the ratios of elemental chromium to zinc in the coating layers are 0.15, 0.09, and 0.21 for EZP1, EZP2, and EZP3, respectively. The Cr content in the chromate layers increased in the order EZP2 < EZP1 < EZP3. The ratio varies depending on the type of zinc-bath additive.

As shown by the profiles from the XRD measurements in the left part of Fig. 3, specimens EZ1, EZ2, and EZ3 exhibit distinct crystallographic orientations of zinc grains. This therefore underlines the effects of organic additives in controlling the crystallographic structures. The (100) and (110) planes appear to be preferentially orientated perpendicular to the surface normal direction in EZ1 and EZ3, respectively. On the other hand, the surface of EZ2 is dominated by both (100) and (110) planes. These distinctions in texture development reflect apparent differences in the surface morphology of the zinc coating layers of different groups, as shown in Fig. 4.

Considering the XRD profiles of EZP2 and EZP3 (right of Fig. 3) in comparison with their EZ counterparts (left of Fig. 3), some modification of the crystallographic orientations of the zinc layer via the chromate conversion process is observed. Specifically, the (100) and (101) orientations are favored in these deposits after chromating. Furthermore, the crystallographic structures of the zinc coatings of EZP2 and EZP3 are comparable, whereas that of EZP1 shows a strong (100) texture.

3.2. Corrosion Behavior

3.2.1. Surface Appearance

Figure 5 shows the surface appearance of the test specimens following the cyclic exposure corrosion test at each stage. In general, a formation of white rust due to oxidation of zinc, which was found to consist mainly of simonkolleite (right of Fig. 3), became increasingly dispersed over time. Subsequently, many of the specimens further developed red rust spots on their surfaces. All specimens in the EZ groups exhibited white rust formation as early as the first week of the test, with red rust developing by the third week. On the other hand, the trivalent chromate coated EZP1 and EZP3 are characterized by a relatively slow rate of rust formation. Red rust developed in the sixth week for EZP1 and was not visibly present in EZP3 at the end of the test. The surface of EZP2, however, appears comparable to those in the EZ groups in each period, with white and red rust forming during the early period.

3.2.2. Anodic Stripping

Six samples of each coating were exposed in the cor-

![Fig. 2. Cross-sectional SEM micrograph of electrogalvanized sample with steel substrate, zinc layer, and chromium conversion layer.](image)

Table 1. The additives for zinc electrodeposition with and without chromate and the corresponding initial thicknesses measured by XRF.

| Sample Set | Additives | Chromate | Initial thickness (μm) |
|------------|-----------|----------|-----------------------|
|            |           |          | 1 wk  | 2 wk  | 3 wk  | 4 wk  | 5 wk  | 6 wk  | Avg. |
| EZ1        | imidazole and epihalohydrin | –       | 8.7   | 8.2   | 7.3   | 7.3   | 8.5   | 8.6   | 8.1   |
| EZ2        | polyquaternary amine salt | –       | 9.3   | 9.6   | 9.0   | 8.9   | 10.2  | 9.0   | 9.3   |
| EZ3        | polyethyleneimine | –       | 10    | 9.9   | 10.2  | 10.2  | 10.4  | 10.5  | 10.2  |
| EZP1       | imidazole and epihalohydrin | Cr³⁺    | 7.0   | 8.0   | 10.1  | 10.6  | 10.2  | 10.4  | 9.4   |
| EZP2       | polyquaternary amine salt | Cr³⁺    | 7.4   | 7.4   | 9.4   | 9.4   | 7.8   | 7.8   | 8.2   |
| EZP3       | polyethyleneimine | Cr³⁺    | 9.6   | 9.6   | 9.7   | 10.2  | 10.1  | 10.4  | 9.9   |
After the corrosion test, the initial thickness of each sample was determined by XRF, as shown in Table 1. The corrosion test was performed for six weeks. One sample of each of the zinc coatings was removed from the chamber every week to obtain the anodic stripping curve. The thickness loss due to corrosion was calculated by subtracting the obtained remaining thickness from the initial thickness shown in Table 1. Changes in the thickness of EZ and EZP group samples are plotted in Fig. 6. In this study, the initial and remaining thicknesses were estimated by XRF and anodic stripping, respectively. Accordingly, a measurement error of 0.5–1 μm should be expected in the thickness loss data.

The coating thickness loss of all EZ specimens increased monotonically and similarly. Zinc in the coating layers of EZ1 and EZ2 samples was all corroded after the fourth and sixth week, respectively. Small amounts of zinc coating remained on EZ3 samples after six weeks. The corrosion rates of the EZ group appear to be similar, considering that EZ3 had a slightly thicker initial coating than EZ1 and EZ2 (Table 1). On the other hand, the EZP groups with chromate were highly corrosion resistant, especially EZP1 and EZP3.

Fig. 3. XRD profiles of the non-chromated samples (A) and chromated samples (B) before and after six week corrosion test.

Fig. 4. SEM micrographs of electrogalvanized samples: EZ1 (A), EZ2 (B), and EZ3 (C).
In light of the measurement error, the corrosion rate of EZP1 appears to be almost negligible during the first few weeks, after which slight zinc corrosion occurred. For EZP3, during the six-week corrosion test, the coating loss was negligible, indicating that the chromate coating of EZP3 works very well as a barrier layer.

3.2.3. Impedance Characteristics

EIS measurements performed on the test specimens following each week of the cyclic exposure corrosion tests resulted in the Bode diagrams representatively shown in Figs. 7 and 8 for the results from the first and sixth weeks. EIS was performed in 10 mM NaCl solution to evaluate the protectiveness of the zinc corrosion products formed in the
corrosion test for the EZ group, and of chromate films for the EZP group. As testing continued, the impedance amplitude was found to reduce progressively for EZ1 and EZP1, remain fairly stable for EZP3, and gradually increase for EZ2, EZP2, and EZ3. The obtained impedance spectra were found to fit well to one of the two equivalent circuits shown in Fig. 9. Figure 9(A) is a simple equivalent circuit consisting of solution resistance $R_s$, charge transfer resistance $R_{ct}$, and a constant phase element (CPE$_{dl}$, CPE$_{dl}$) for the electric double layer. In another equivalent circuit, shown in Fig. 9(B), film resistance $R_f$ and a constant phase element (CPE$_{f}$, CPE$_{f}$) for corrosion products or chromate films are added to the equivalent circuit shown in part A. Circuit A was used for curve-fitting only at the early stage of corrosion. $T$ and $\alpha$ are the CPE magnitude and exponent, respectively. The corresponding equivalent circuit elements are summarized in Table 2.

The reciprocal of the charge transfer resistance, $R_{ct}^{-1}$, is taken as an index of corrosion rate, and is plotted vs time for the EZ and EZP groups in Figs. 10(A) and 10(B), respectively. The $R_{ct}^{-1}$ values for the EZ group are similar and are in the range $5 \sim 15 \times 10^{-5}$ $\Omega^{-1}$ cm$^{-2}$. Only EZ1 shows a higher value ($30 \times 10^{-5}$ $\Omega^{-1}$ cm$^{-2}$) at the final stage (sixth week). According to the EIS data for the EZ group, their corrosion rates are similar, although EZ1 has a slightly higher corrosion rate at the final stage, which is probably due to the onset of corrosion of the underlying steel. This EIS result for the EZ group is consistent with that obtained by anodic stripping. On the other hand, in the EZP group (Fig. 10(B)), EZP3 exhibits excellent corrosion resistance until the end of the corrosion test, indicating that the chromate film for EZP3 is moderately effective in protecting the

---

**Table 2.** Equivalent circuit elements obtained by curve-fitting to the equivalent circuits in Fig. 9 for the non-chromated and chromated electrogalvanized samples at the first and sixth weeks of the cyclic exposure test. $T$ and $\alpha$ are the CPE magnitude and exponent, respectively.

| Sample | $R_s$ (\Omega cm$^2$) | $R_f$ (\Omega cm$^2$) | $R_{ct}$ (\Omega cm$^2$) | $T_{dl}$ (\mu F cm$^{-1}$ s$^{(1-\alpha)}$) | $\alpha_{dl}$ | $T_f$ (\mu F cm$^{-1}$ s$^{(1-\alpha)}$) | $\alpha_f$ |
|--------|----------------------|----------------------|----------------------|---------------------------------|------------|---------------------------------|------------|
| EZ1    | wk1 150              | –                    | 13 000               | 210                             | 0.56       | –                               | –          |
|        | wk6 220              | 310                  | 3 500                | 2 300                           | 0.74       | 500                             | 0.46       |
|        | wk1 220              | 7 400                | –                    | 810                             | 0.50       | –                               | –          |
| EZ2    | wk6 200              | 220                  | 9 800                | 1 400                           | 0.72       | 380                             | 0.59       |
|        | wk1 150              | 5 100                | –                    | 540                             | 0.74       | –                               | –          |
| EZ3    | wk6 350              | 240                  | 15 000               | 1 300                           | 0.72       | 170                             | 0.59       |
|        | wk1 230              | –                    | 80 000               | 31                              | 0.78       | –                               | –          |
| EZP1   | wk6 310              | 320                  | 5 800                | 830                             | 0.55       | 120                             | 0.47       |
|        | wk1 100              | –                    | 9 700                | 420                             | 0.42       | –                               | –          |
| EZP2   | wk6 310              | 230                  | 12 000               | 1 300                           | 0.66       | 250                             | 0.58       |
|        | wk1 210              | –                    | 12 000               | 35                              | 0.79       | –                               | –          |
| EZP3   | wk6 350              | 17 000               | 18 000               | 120                             | 0.87       | 56                              | 0.58       |
zinc coating. The $R_{ct}^{-1}$ for EZP1 indicates high corrosion resistance as with EZP3 at the initial stage (until 2 weeks), and then starts to increase after three weeks. This indicates that the chromate is effective only for two weeks and will deteriorate after further exposure. The EZP2 chromate corroded rapidly during the first week of exposure. Also, for the EZP group, the degradation trend shown by EIS is consistent with that obtained by anodic stripping. The degradation of the zinc coatings with and without chromate can be successfully evaluated by the non-destructive EIS method.

### 3.3. Effect of Additives

Additives are generally added to electroplating baths to improve the quality and uniformity of the zinc coatings.\(^{25}\) Particularly, additives serve as adsorbates, which are selectively transferred from the electrolyte to the cathode surface. Often, the additive molecules are preferentially adsorbed at rapid growth sites and locally hinder the reduction of metal ions, resulting in a decrease in the overall growth rate of metal coatings.\(^{26}\) This explains why the thickness of zinc coatings is affected by additives, despite the same amount of electric charge being supplied during the zinc electroplating. Adsorption of the additives also contributes to a reduction in the mean free path of the adions and influences the nucleation, grain growth, and texture development of the crystalline metals.\(^{12,13,27}\)

The three organic additives examined herein exhibit different levels of charge density in the order polyquaternary amine salt < imidazole and epihalohydrin < polyethyleneimine.\(^{11}\) A higher charge density of additives results in stronger adsorption on the deposit, slowing down the growth of dendrites and modifying the crystallographic orientation. It can be anticipated that their adsorption strength varies correspondingly and that these additives influence the texture development of the zinc coatings in different ways. Indeed, as presented in Figs. 3 and 4, the electrogalvanized coating samples exhibited distinct textures and surface morphologies when different additives were employed.

The dissolution rate of zinc will be dependent on the crystallographic plane.\(^{29}\) A close-packed plane is the most stable. The EZ group samples showed different planes (Fig. 3(A)); however, the corrosion rates of the samples from the three groups were similar. This may be attributed to the aggressive corrosion test conditions employed.

A trivalent chromate conversion coating layer is formed on a zinc coating surface through an oxidation-reduction process, which comprises zinc dissolution and complex chromium compound film formation steps.\(^{29,30}\) Zinc dissolves due to acidic attack from the trivalent chromate bath, and the dissolved zinc precipitates to form a chromate layer. Since the surface metal of the electrogalvanized layer directly interacts with chromic acid and chromium salt solutions, and is thus primarily involved in these chromating steps, it can be anticipated that the characteristics of the zinc layer will influence the development of a chromate conversion coating layer and hence affect the corrosion behavior of the film.

Indeed, it is determined that EZP1, EZP2, and EZP3, which have distinct crystallographic textures and surface morphologies in their zinc coating layers, exhibit marked differences in the relative Cr contents in their films and in the corresponding degrees of corrosion resistance, in the order EZP2 < EZP1 < EZP3. This is achieved despite using the same chemicals and processing parameters for the chromate conversion treatment in preparing these materials. The corrosion resistance corresponds to the plane packing density. Narin et al.\(^{31}\) showed that zinc layers with (110) and (100) textures promoted the formation of amorphous oxide and amorphous layers, respectively. The formation of a relatively thick amorphous-oxide layer, resulting from the crystallographic texture of zinc, enhances the corrosion resistance of the chromate films. The relatively high Cr content in the trivalent chromate film of EZP3 could stem from the crystallographic texture of its galvanized layer, which facilitates zinc dissolution and chromate conversion.\(^{12,29,32}\) EZP3, in particular, exhibited a high charge transfer resistance, which suggests a more protective and stable chromate film.\(^{13}\) Consequently, EZP3 withstood a corrosion attack relatively well compared to all sets of the specimens throughout the six-week test period. This result therefore emphasizes that the corrosion resistance of electrogalvanized coatings is critically influenced by the trivalent chromate treatment, which is in turn affected by organic additives in the zinc plating baths and the formation of the zinc coating layer.

### 4. Conclusions

This study has demonstrated the use of electrochemical techniques to evaluate the corrosion resistance of galvanized steels. The degradation of zinc coatings is successfully evaluated by non-destructive EIS. The results showed that organic additives used in the electrodeposition of galvanized coatings play an important role in controlling both the structure of the zinc layer and the formation of the trivalent chromate conversion film. This subsequently influences the level of corrosion resistance in the coatings, as observed in
a wet-dry cyclic saline environment. Among the organic additives in the polyamine group under investigation, polyethyleneimine provided a relatively high level of corrosion resistance for electrogalvanized coatings with conversion layer. The high chromium content in the trivalent chromate conversion coating layer and the structure of the zinc layer that promotes the formation of protective corrosion products are potential key factors responsible for the improved corrosion resistance.

Acknowledgments

The grant for the Surface Coatings Technology for Metals and Materials Research Unit (GRU 6000162001-1) and the grant for International Research Integration: Chula Research Scholar, Ratchadaphiseksomphot Endowment Fund (GCRS-58-02-21-01) are gratefully acknowledged. TW also would like to thank the 90th Anniversary of Chulalongkorn University Fund and Overseas Research Experience Scholarship for Graduate Student for the financial support.

REFERENCES

1) F. W. Eppensteiner and M. R. Jennkind: *Met. Finish.*, 105 (2007), 413.
2) C. R. Tomachuk, C. I. Elsner, A. R. Di Sarli and O. B. Ferraz: *Mater. Chem. Phys.*, 119 (2010), 19.
3) A. R. Di Sarli, J. D. Culcasi, C. R. Tomachuk, C. I. Elsner, J. M. Ferreira, Jr. and I. Costa: *Surf. Coat. Technol.*, 258 (2014), 426.
4) M. Ely, I. Światowska, A. Seyeu, S. Zanna and P. Marcus: *J. Electrochem. Soc.*, 164 (2017), C276.
5) K. G. N. Ramesh Bapu, G. Devaraj and J. Ayyapparaj: *J. Solid State Electrochem.*, 3 (1998), 48.
6) N. Zaki: *Met. Finish.*, 105 (2007), 425.
7) J. García-Antón, R. M. Fernández-Domene, R. Sánchez-Tovar, C. Escrivá-Cerdán, R. Leiva-García, V. Garcia and A. Urtiaga: *Chem. Eng. Sci.*, 111 (2014), 402.
8) B. Kavitha, P. Santosh, M. Renukadevi, A. Kalpana, P. Shakhthivel and T. Vasudevan: *Surf. Coat. Technol.*, 201 (2006), 3438.
9) M. Esfahani, J. Zhang, Y. Durandet, J. Wang and Y. C. Wong: *J. Electrochem. Soc.*, 163 (2016), D476.
10) J.-C. Hsieh, C.-C. Hu and T.-C. Lee: *J. Electrochem. Soc.*, 155 (2008), D675.
11) J.-C. Hsieh, C.-C. Hu and T.-C. Lee: *Surf. Coat. Technol.*, 203 (2009), 3111.
12) K. O. Nayana and T. V. Venkatesha: *J. Electroanal. Chem.*, 663 (2011), 98.
13) J. Ortiz-Aparicio, Y. Meas, G. Trejo, R. Ortega, T. Chapman and E. Chaintet: *J. Appl. Electrochem.*, 43 (2013), 289.
14) M. S. Chandrasekar, S. Srinivasan and M. Pushpavanam: *J. Mater. Sci.*, 45 (2010), 1160.
15) R. Ramanauskas, P. Quintana, L. Maldonado, R. Pomés and M. A. Pech-Canul: *Surf. Coat. Technol.*, 92 (1997), 16.
16) C. R. Tomachuk, C. I. Elsner, A. R. Di Sarli and O. B. Ferraz: *J. Coat. Technol. Res.*, 7 (2010), 493.
17) R. Kriegl, A. Vimalanandan and M. Rohwerder: *J. Electrochem. Soc.*, 161 (2014), C156.
18) M. Mouanga, L. Ricq, J. Douglaide and P. Berçot: *J. Appl. Electrochem.*, 37 (2007), 283.
19) M. S. Chandrasekar and P. Malathy: *Mater. Chem. Phys.*, 124 (2010), 516.
20) A. Nishikata, Y. Yamashita, H. Katayama, T. Tsaru, A. Usami, K. Tanabe and H. Mabuchi: *Corros. Sci.*, 37 (1995), 2059.
21) G. A. El-Mahdy, A. Nishikata and T. Tsaru: *Corros. Sci.*, 42 (2000), 183.
22) A. P. Yadav, A. Nishikata and T. Tsaru: *Corros. Sci.*, 46 (2004), 169.
23) W. Han, C. Pan, Z. Wang and G. Yu: *Corros. Sci.*, 88 (2014), 89.
24) A. P. Yadav, A. Nishikata and T. Tsaru: *Corros. Sci.*, 46 (2004), 361.
25) M. Pushpavanam: *J. Appl. Electrochem.*, 36 (2006), 315.
26) M. Paunovic and M. Schlesinger: Fundamentals of Electrochemical Deposition, Wiley, Hoboken, NJ, (2006), 177.
27) R. F. Ashton and M. T. Hepworth: *Corrosion*, 24 (1968), 50.
28) M. P. Gigandet, J. Faucheu and M. Tachez: *Surf. Coat. Technol.*, 89 (1997), 285.
29) A. Pirnát, L. Mészáros and B. Lengyel: *Electrochim. Acta*, 35 (1990), 515.
30) N. Jantaping, C. A. Schuh and Y. Boonyongmaneerat: *Surf. Coat. Technol.*, 329 (2017), 120.
31) H. Park and J. A. Szpunar: *Corros. Sci.*, 40 (1998), 525.
32) T. Bellezze, G. Roventi and R. Fratesi: *Surf. Coat. Technol.*, 155 (2002), 221.