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Corrosion resistance of compositionally modulated multilayered Zn–Ni alloys deposited from a single bath

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Abstract

By consecutive deposition at two different current densities from a single sulfate–chloride bath, compositionally modulated multilayered (CMM) coatings of Zn–Ni alloys, with different number, thickness and sequence of the sublayers were obtained. The corrosion resistance of the coatings was studied by potentiodynamic dissolution and by corrosion potential measurement. In the current–potential (stripping) curves two well-defined peaks were observed. With increase in the number of sublayers, regardless of their individual thickness, the correlation between the amount of Zn, dissolved at more negative potentials and the whole amount of the metal in the CMM coatings, decreases. The corrosion potentials of CMM coatings are most positive (−0.940 V vs SSE) when they end with a Zn–Ni18% oversublayer. As a result of the alternation of Zn–Ni alloy sublayers with different Ni content the obtained CMM coatings have increased corrosion resistance in comparison with the monolayer coatings of the composing alloys.

1. Introduction

Compositionally modulated multilayers (CMM) are coatings which consist of a number of layers each composed of two sublayers of different metals or alloys [1]. By deposition at different current densities from a single bath containing ions of two metals it is possible to be obtained CMM coatings consisting of alloys with different composition [2–24]. Kalantary et al. [25] deposited Zn–Ni multilayered coatings on a rotating cylinder electrode from a sulfate electrolyte. By changing the current density and the electrode rotation speed, the alloy composition was controlled. In the current density range 1–50 A dm^{-2} the Ni content was between 3 and 14% and in the range 100–130 A dm^{-2} it was 20–30%. Jongzhong et al. [26] obtained compositionally modulated Zn–Fe multilayered coatings from chloride electrolyte and studied the influence of current density and stirring on their composition. Kirilova et al. [27] studied one and two-layer coatings [27] and CMM coatings of Zn–Co1% and Zn–Co6.5% alloys [28]. During the anodic dissolution of the two-layer coating composed of Zn–Co1% and Zn–Co6.5% layers three anodic current peaks were observed due to the dissolution of pure Zn and of Zn–Co alloy phases. The peak heights and the potentials of their maxima did not depend on the order of the layers but only on their thickness [27]. These authors established that with increase in the sublayer number, regardless of the individual thickness and sequence, the dissolution potentials of CMM coatings shifted in the positive direction approaching the dissolution potentials of pure Co [28]. Kirilova and Ivanov [29] studied the corrosion behaviour of Zn–Co CMM by corrosion potential measurement and neutral salt spray (NSS) test. The corrosion potential of a coating deposited from a single bath was more positive than that of a coating deposited from dual baths with the same number and thickness of the sublayers. The corrosion resistance of the coatings deposited from a single bath was higher than that of the coatings deposited from dual baths. In chromated CMM coatings with the Zn–Co1% oversublayer no red rust appeared on their surface even after 1584 h of salt spray corrosion test. Their corrosion resistance, with regard to the appearance of both white and red rust was higher than that of pure Zn or Zn–Co0.8% alloy coatings. Non-chromated CMM coatings consisting of a great number of thin sublayers were more corrosion resistant than CMM coatings consisting of a small number thick sublayers with the same total thickness.

The aim of this study is to deposit from a single bath smooth and bright multilayered coatings of Zn–Ni alloys and to study their corrosion resistance by anode potentiodynamic dissolution of the coatings and by corrosion potential measurement.

2. Experimental details

Multilayers were deposited and potentiodynamically dissolved (stripped) in two equal tri-electrode glass cells. The cathode was a 1 cm^2 copper (or platinum) plate and both anodes were 2 cm^2 platinum plates. The samples, for the corrosion potential determination, were deposited on a copper substrate with 4 cm^2 surface area. The cathode surface was polished with emery paper (grit 600), degreased in an ultrasonic UM-2 bath and then etched in 1:1 HNO_3 (only the copper one). The cathodic potential was measured relative to a mercury sulfate reference electrode (SSE) of potential +0.670 V vs NHE. The galvanostatic deposition of Zn–Ni alloy CMM coatings was carried out by successive switching on the two galvanostats (TEC7M).

CMM coatings were deposited from an electrolyte containing 88 g dm^{-3} $ZnSO_4 \cdot 7H_2O$, 775 g dm^{-3} $NiSO_4 \cdot 7H_2O$, 57 g dm^{-3} $NiCl_2 \cdot 6H_2O$, 45 g dm^{-3} H_3BO_3, 44 g dm^{-3} $(NH_4)_2SO_4$ and the commercial additives AZ-1 (50 cm^3 dm^{-3}), composed of ethoxylated alcohol (with a general formula $R{-}O{-}(CH_2CH_2O)_nH$, where R is an alkyl or alkylaryl radical with 1–20 carbon atoms in the alkyl group and n is from 3 to 30) and of a Na or K salt of benzoic acid, AZ-2 (10 cm^3 dm^{-3}), composed of benzylidene acetone and ethanol, 6 g dm^{-3} saccharin, 20 cm^3 dm^{-3} 30% solution of hydroxytilated butyn-2-diol-1,4 (EAA) and 2 mg dm^{-3} Na-decylsulphate (EFAP). The pH of the electrolyte was 2.5. The temperature of the electrolyte was 50 ± 1 °C and was kept constant with a UH-16 thermostat.

CMM coatings, consisting of sublayers with different composition, number and sequence were deposited. The coatings consisting of even number of sublayers begin with one Zn–Ni alloy sublayer and finish with the other Zn–Ni alloy sublayer. The coatings, consisting of odd number of sublayers begin and finish with sublayer of one and the same alloy.

CMM coatings were composed from the following pairs of alloy sublayers:

0.5 μm Zn–Ni3.5% + 0.5 μm Zn–Ni5%,
1.0 μm Zn–Ni5% + 1.2 μm Zn–Ni18% and
4.0 μm Zn–Ni5% + 4.8 μm Zn–Ni18%

The alloy sublayers were deposited at current densities as follows: 0.5 μm Zn–Ni3.5% – at 2 A dm^{-2} for 2.5 min, 0.5 μm Zn–Ni5% – at 5 A dm^{-2} for 1 min and 0.5 μm Zn–Ni18% – at 10 A dm^{-2} for 0.5 min. The deposition time for 1.0–1.2 μm thick coatings was two times and for 4.0–4.8 μm thick coatings eight times longer, respectively. The thickness of the sublayers was determined by measuring the amount of electricity consumed for their dissolution and using Faraday's laws. In the whole range of densities, smooth, light-grey and semi-bright coatings were obtained. It was found out that the individual sublayer composition does not change with electroplating time.

The potentiodynamic stripping was carried out at 25 ± 1 °C in an electrolyte containing 75 g dm^{-3} $ZnSO_4 \cdot 7H_2O$, 22 g dm^{-3} $(NH_4)_2SO_4$ and 30 g dm^{-3} H_3BO_3. It was carried out within the potential range −1.5 to +0.5 V vs SSE at scan rate of 2 mV s^{-1} using a potentiostat (EP20A Elpan) and scanner (EG20 Elpan). The current–potential dependence (stripping curve) was registered on a X–Y plotter (Endim 622.01) [30–44].

The corrosion potentials of the coatings were measured at open electric circuit in an electrolyte with pH = 6, containing 6 g dm^{-3} NaCl and 94 g dm^{-3} Na_2SO_4. The potentials were registered at a room temperature after 24 h.

In all experiments the current was measured with an ammeter ML10, and the cathodic potential with a digital voltmeter (V542.1) [6–10].

3. Results and discussion

3.1. *Surface appearance and surface and cross-sectional morphology*

The CMM coatings produced under the above conditions were characterized by their top layer surface appearance and surface and cross-sectional morphology which were examined on a JSM 5300 scanning electron microscope (SEM). The coatings were gray and semi-bright and surface blemishes were not observed with the naked eye. Figure 1 shows the cross-sectional morphology of a CMM coating, composed of five 5.0 μm Zn–Ni18% alloy sublayers (light strips) and five 5.0 μm Zn–Ni5% alloy sublayers (dark strips). The specimen shows cracks between sublayers attributable to mechanical damage that occurred during the preparing of the cross-sections by metallographic techniques. A bad contrast between the sublayers is observed because of the little difference in the Ni content of the composing alloys. Figure 2 shows the surface morphology of the CMM coatings composed of 5.0 μm Zn–Ni5% and 5.0 μm Zn–Ni18% alloy sublayers ending with a 5.0 μm Zn–Ni18% oversublayer. It is observed that the coatings

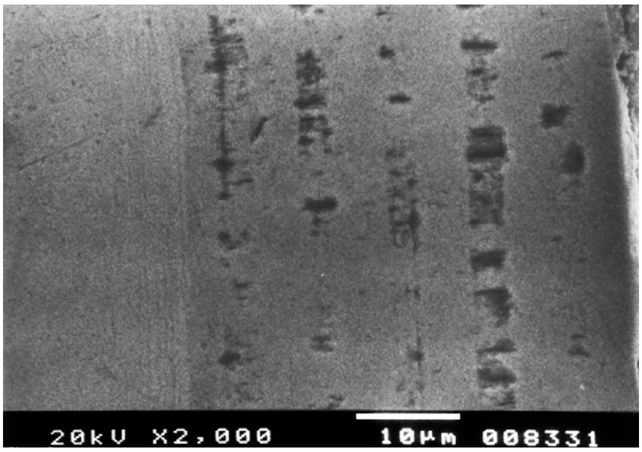

Fig. 1. Cross-sectional morphology of Zn–Ni5% + Zn–Ni18% CMM coating.

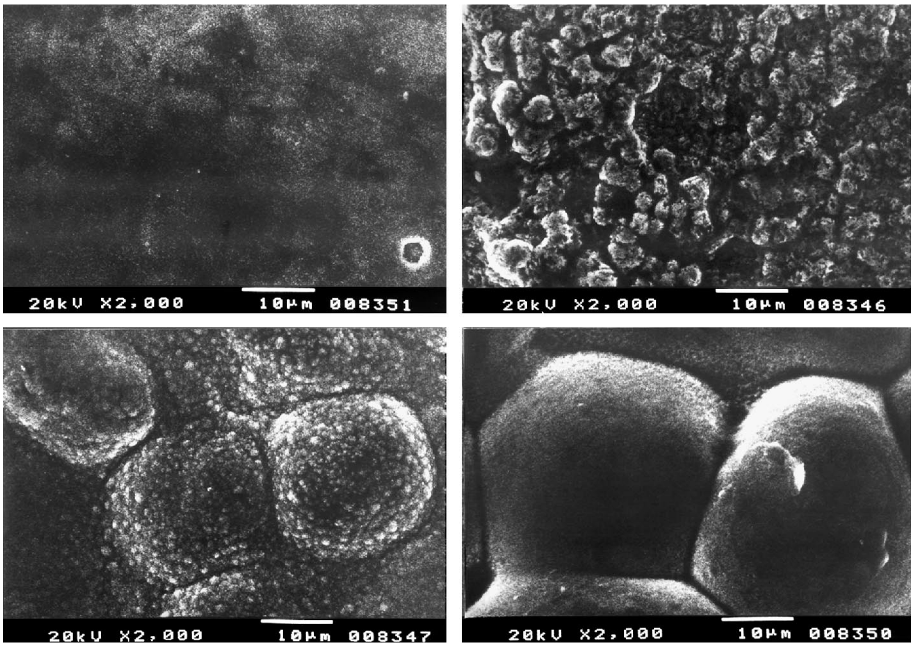

Fig. 2. Surface morphology of 5 μm Zn–Ni5% + 5 μm Zn–Ni18% CMM coatings ending with a 5 μm Zn–Ni18% oversublayer, composed of: (a) 1 sublayer; (b) 2 sublayers; (c) 3 sublayers; (d) 4 sublayers.

are smooth, fine-grained and without pores on the surface. With increase in the number of sublayers nodular structures are formed.

3.2. *Potentiodynamic stripping of monolayer Zn–Ni alloy coatings with different composition*

In Figure 3 are presented the stripping curves of one-layer alloy coatings, deposited at current densities: 2 A dm^{-2} (3.5 wt.% Ni) for 15 min (curve 1); 5 A dm^{-2} (5 wt.% Ni) for 10 min (curve 2) and 10 A dm^{-2} (18 wt.% Ni) for 2 min (curve 3). Two peaks (at −1.150/−1.250 V and at −0.600/−0.700 V) appear on the stripping curves of the coatings, deposited at 2 or 5 A dm^{-2} and only one large peak at −0.850 V appears on the stripping curve of the coating, deposited at 10 A dm^{-2}. Consequently, the corrosion resistance of the alloys, composing the CMM coatings, increases with increase of the Ni content.

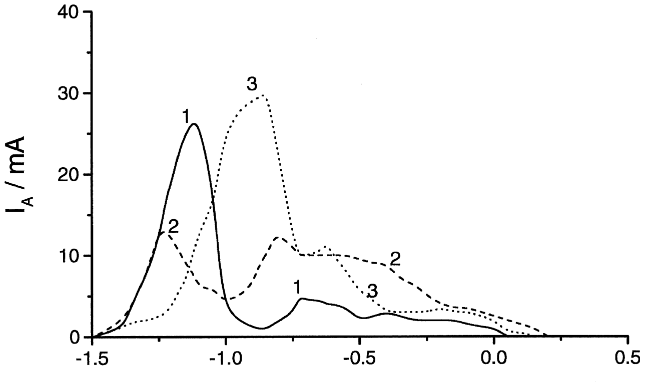

Fig. 3. Striping voltammograms of coatings deposited from a single bath at a current density of: (1) 2 A dm^{-2}, $\tau = 15$ min; (2) 5 A dm^{-2}, $\tau = 10$ min; (3) 10 A dm^{-2}, $\tau = 2$ min. Scanning rate 2 mV s^{-1}.

3.3. *Potentiodynamic stripping of CMM Zn–Ni alloy coatings with different composition*

The corrosion resistance of the CMM coatings consisting of different number, sequence and thickness of Zn–Ni alloy sublayers with different Ni content was studied by stripping in potentiodynamic regime. The obtained stripping curves are similar to those presented in Figure 3. Two separate peaks are observed on the stripping curves corresponding to the dissolution of alloys with different corrosion resistance.

By graphical integration, the area included between the axis of potential development and the whole stripping curve was determined, revealing the quantity of electricity (q/Coulombs) required for the dissolution of the whole CMM coating. Similarly, the area included between the axis of potential development and the stripping peak at more negative potential was determined, revealing the quantity of electricity (q^{I}/Coulombs) required for the dissolution of a part of the less corrosion resistant metal – zinc. The correlation q^{I}/q characterizes the corrosion resistance of the CMM coatings. With decrease of q^{I}/q the corrosion resistance increases.

Figure 4 shows the dependence of q^{I}/q on the number of sublayers for CMM coatings consisting of 0.5 μm Zn–Ni3.5% and 0.5 μm Zn–Ni5% alloy sublayers. It is seen that for coatings ending with a Zn–Ni3.5% oversublayer (curve 2) the correlation q^{I}/q is two times larger than for coatings ending with a Zn–Ni5% oversublayer (curve 1), i.e. the corrosion resistance of

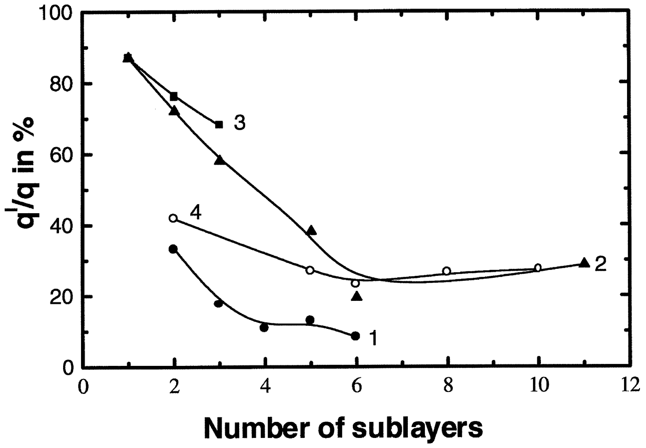

Fig. 4. Dependence of the correlation between the quantity of Zn dissolved at more negative potential and the whole quantity of metal in the coating (q^{I}/q) on the number of sublayers. CMM coatings consisting of 0.5 μm Zn–Ni3.5% and 0.5 μm Zn–Ni5% sublayers. (1) Coatings ending with a 0.5 μm Zn–Ni5% oversublayer; (2) coatings ending with a 0.5 μm Zn–Ni3.5% oversublayer; (3) coatings of Zn–Ni3.5%; (4) coatings of Zn–Ni5%.

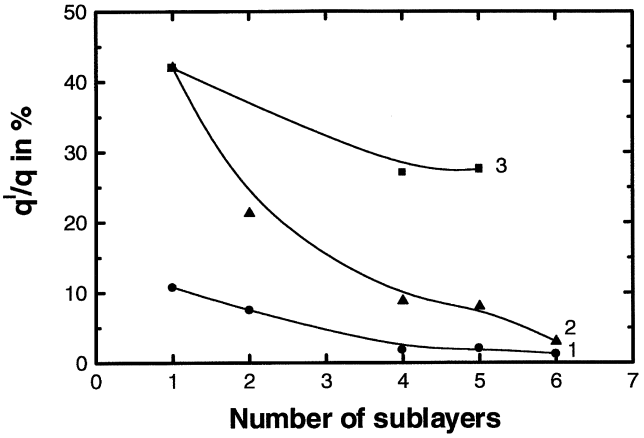

Fig. 5. Dependence of the correlation between the quantity of Zn dissolved at more negative potential and the whole quantity of metal in the coating (q^{I}/q) on the number of sublayers. CMM coatings consisting of 1.0 μm Zn–Ni5% and 1.2 μm Zn–Ni18% sublayers. (1) Coatings of Zn–Ni18% and coatings ending with a 1.2 μm Zn–Ni18% oversublayer; (2) coatings ending with a 1.0 μm Zn–Ni5% oversublayer; (3) coatings of Zn–Ni5%.

coatings depends on the Ni content of the oversublayers. In both cases the correlation q^{I}/q is two (curve 2) or six (curve 1) times less than that for Zn–Ni3.5% coatings with the same thickness (curve 3). This correlation for CMM coatings ending with a Zn–Ni5% oversublayer (curve 1) is three times less than that for Zn–Ni5% coatings with the same thickness (curve 4). Curves 1 and 2 show that the corrosion resistance of the CMM coatings with Ni content practically equal to that in the composing alloys, is increased as a result of the alternation of the Zn–Ni sublayers.

Figure 5 shows the same dependence for CMM coatings, consisting of 1.0 μm Zn–Ni5% and 1.2 μm Zn–Ni18% alloy sublayers. Curve 1 showing this dependence for coatings ending with a Zn–Ni18% oversublayer lies lower than curve 2, showing that dependence for coatings ending with a Zn–Ni5% oversublayer. With increase in the number of sublayers the difference between curves 1 and 2 decreases. Both curves lie lower than the curve of the correlation q^{I}/q for Zn–Ni5% alloy coatings (curve 3). Curve 1 coincides with the curve of the correlation q^{I}/q for Zn–Ni18% alloy coatings with the same thickness (curve 4). In this case as a result of the alternation of the alloy sublayers the CMM coatings, with lower Ni content, have increased corrosion resistance in comparison with the composing alloys.

Figure 6 shows the same dependence for CMM coatings consisting of four times thicker sublayers, i.e. 4 μm Zn–Ni5% and 4.8 μm Zn–Ni18%. In this case the differences between curves 1 and 2, result of the different Ni content of the oversublayers, almost disappear. Figure 6 shows that the increase of the individual sublayer thickness does not lead to the substantial decrease of the correlation q^{I}/q, i.e. does not improve the corrosion resistance of the multilayered coatings.

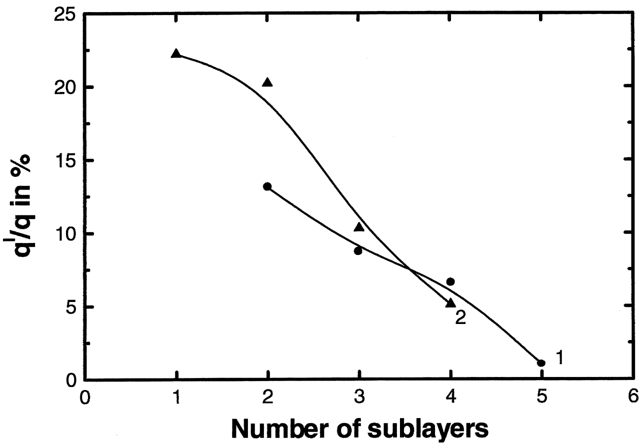

Fig. 6. Dependence of the correlation between the quantity of Zn dissolved at more negative potential and the whole quantity of metal in the coating (q^{I}/q) on the number of sublayers. CMM coatings consisting of 4.0 μm Zn–Ni5% and 4.8 μm Zn–Ni18% sublayers. (1) Coatings ending with a 4.8 μm Zn–Ni18% oversublayer; (2) coatings ending with a 4.0 μm Zn–Ni5% oversublayer.

3.4. *Definition of corrosion potentials*

Table 1 shows corrosion potentials of coatings of Zn–Ni3.5% and Zn–Ni18% alloys and CMM coatings composed of five sublayers ending either with a Zn–Ni3.5% or Zn–Ni18% oversublayer. The potential of pure Zn (−1.415 V) is the most negative and the deposit is corroded to the Cu substrate. The corrosion potential becomes more positive with increase of Ni content in the alloy coating (−1.140 V for Zn–Ni3.5% and −0.950 V for Zn–Ni18%). The coating with 3.5 wt.% Ni is covered with white rust and that with 18 wt.% Ni is grey and without rust on the surface. The multilayered coating, ending with a Zn–Ni3.5% oversublayer, containing 9.3 wt.% Ni, has corrosion potential −1.040 V,

Table 1. Values of the corrosion potentials E_{corr}/V vs SSE of CMM coatings composed of Zn–Ni3.5% and Zn–Ni18% alloys deposited from a single bath after 24 h exposition in solution containing 94 g dm^{-3} Na_2SO_4 and 6 g dm^{-3} NaCl in dependence on the number, sequence and thickness of sublayers

Type of CMM	Number of sublayers	Average Ni content /wt.%	E_{corr} /V vs SSE
[0.6 μm Zn–Ni18%]$_5$	5	18	−0.950
[0.5 μm Zn–Ni3.5%]$_5$	5	3.5	−1.140
[0.6 μm Zn–Ni18% + 0.5 μm Zn–Ni3.5%]$_2$ + 0.6 μm Zn–Ni18%	5	12.2	−0.940
[0.5 μm Zn–Ni3.5% + 0.6 μm Zn–Ni18%]$_2$ + 0.5 μm Zn–Ni3.5%	5	9.3	−1.040
[0.6 μm Zn]$_6$	6	0	−1.415

which is more positive than that of the one-layer coating of alloy Zn–Ni3.5% (−1.140 V) and the amount of the white rust on the surface is less. The corrosion potential of CMM coating ending with a Zn–Ni18% oversublayer containing 12.2 wt.% Ni (−0.940 V) coincides with that of one-layer coating of alloy Zn–Ni18% (−0.950 V) and the surface is grey without rust on it. Consequently, the corrosion resistance of the coatings increases due to the alteration of sublayers with different Ni content. The monolayer coating containing 3.5 wt.% Ni corrodes fastest and the multilayered coating ending with a Zn–Ni18% oversublayer shows maximum corrosion resistance.

4. Conclusions

By consecutive deposition at two different current densities from sulfate–chloride electrolyte containing Zn^{2+} and Ni^{2+} in the presence of organic brightening additives smooth and semibright compositionally modulated multilayered Zn–Ni alloys may be obtained.

With increase in the number of sublayers regardless of their individual thickness the correlation between the quantity of Zn, dissolved at more negative potentials and the whole quantity of the metal in the CMM coatings, decreases. The most corrosionally resistant are the multilayered coatings ending with a sublayer containing 18 wt.% Ni and the least resistant are the coatings ending with a sublayer containing 3.5 wt.% Ni.

The corrosion potentials of CMM coatings have the most positive values (−0.940 V) when they end with a Zn–Ni18% sublayer. Such coatings have maximum corrosion resistance.

As a result of the alteration of Zn–Ni alloy sublayers with different Ni content the obtained CMM coatings have increased corrosion resistance in comparison with the monolayer coatings of the composing alloys.

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