Journal of Applied Electrochemistry **29**: 1133–1137, 1999.

Technical note

Corrosion behaviour of Zn–Co compositionally modulated multilayers electrodeposited from single and dual baths

I. KIRILOVA* and I. IVANOV
Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria
*(*author for correspondence, e-mail: kirilova@ipchp.ipc.bas.bg)*

Received 23 February 1998; accepted in revised form 12 January 1999

Key words: cobalt, corrosion, multilayer deposition, zinc

Abstract

The corrosion behaviour of Zn–Co compositionally modulated multilayers (CMM) was studied using corrosion potential measurement and the neutral salt spray (NSS) method. It was established that the corrosion potentials of the CMM, deposited from a single bath, are significantly more positive than those deposited from a dual bath. The best corrosion resistance was found for multilayers consisting of four sublayers, each 3.0 μm thick, deposited both from a dual bath and from a single bath (with an oversublayer of Zn–Co 1%).

1. Introduction

Compositionally modulated multilayers (CMM) are coatings which consist of alternate sublayers of two or more components [1–7]. Such coatings have better corrosion resistance and physicomechanical properties than those observed in common alloys [8–12]. The production and investigation of the properties of CMM composed of Zn and Fe-group metals are of great theoretical and practical interest but data concerning such CMM are very rare [1, 2]. In a previous paper [13], we described the production of Zn–Co CMM by electrodeposition from single and dual baths using electrolytes for deposition of Zn [14], Co [15] and Zn–Co alloyed [16] coatings. Both one and two-layer Zn and Co coatings [17], as well as Zn–Co CMM [13] deposited from single and dual baths were studied by means of anodic stripping of the deposits. It was established that most of the CMM coatings obtained from a dual bath dissolve at potentials close to those for pure Co coatings. CMM coatings obtained from a single bath dissolve at potentials between the dissolution potentials of pure Co and pure Zn coatings. With increase in the number of sublayers in CMM coatings (deposited both from dual and single baths) potentials of the stripping peaks are shifted positively.

The aim of this work is to study the corrosion resistance of Zn–Co CMM obtained from a single bath and also from a dual bath by corrosion potential measurement and neutral salt spray (NSS) test.

2. Experimental details

Zinc and cobalt coatings and Zn–Co CMM were deposited galvanostatically in a conventional glass cell. Fe plates (1 cm^2 surface area) were used in the corrosion potential measurements as cathodes and Pt plates (2 cm^2 surface area) each were used as anodes. The cathodes for the NSS test were Fe plates (70 cm^2 surface area). The anodes for the deposition of Zn coatings were Zn, while the anodes for the deposition of Zn–Co 0.8% alloys and CMM were platinized Ti and Co.

Zn–Co CMM from a dual bath were obtained after consecutive deposition at 2 A dm^{-2} from the following electrolytes. The zinc electrolyte contained 175 g dm^{-3} $ZnSO_4.7H_2O$, 22 g dm^{-3} $(NH_4)_2SO_4$, 30 g dm^{-3} H_3BO_3, 50 cm^3 dm^{-3}AZ-1 (composed of ethoxylated alcohol and of sodium or potassium salt of benzoic acid), and 10 cm^3 dm^{-3}AZ-2 (composed of benzylidene acetone and ethanol). The pH of the bath was 4.5 [18]. The cobalt electrolyte contained 258.5 g dm^{-3} $CoSO_4.7H_2O$, 18 g dm^{-3} $CoCl_2.6H_2O$, 45 g dm^{-3} H_3BO_3, 2 g dm^{-3} saccharin, 5 cm^3 dm^{-3} 30% solution of hydroxyethylated-buthyn-2-diol-1,4(EAA), and 2 mg dm^{-3} Na-decylsulfate (EFAP). The pH of the bath was 2.5.

Zn–Co CMM from a single bath were obtained from an electrolyte containing 175 g dm^{-3} $ZnSO_4.7H_2O$, 258.5 g dm^{-3} $CoSO_4.7H_2O$, 18 g dm^{-3} $CoCl_2.6H_2O$, 22 g dm^{-3} $(NH_4)_2SO_4$, 45 g dm^{-3} H_3BO_3, 50 cm^3 dm^{-3} AZ-1, 10 cm^3 dm^{-3} AZ-2, 2 g dm^{-3} saccharin, 2 mg dm^{-3} EFAP, and 5 cm^3 dm^{-3} 30% solution of EAA. The pH of the bath was 2.5. The alloys Zn–Co 1% and Zn–Co 6.5% were deposited galvanostatically at 0.2 and 2.0 A dm^{-2}, respectively [16].

Zn–Co 0.8% alloy was deposited in an electrolyte containing 180 g dm^{-3} $ZnSO_4.7H_2O$, 80 g dm^{-3} $CoSO_4.7H_2O$, 5 g dm^{-3} $CoCl_2.6H_2O$, 26 g dm^{-3} NH_4Cl, 25 g dm^{-3} H_3BO_3, and additives CK-1 (40 cm^3 dm^{-3}) and CK-2 (2 cm^3 dm^{-3}) [19].

The corrosion potentials of the coatings were measured at open circuit using a digital voltmeter (V 542.1) in an electrolyte containing 6 g dm^{-3} NaCl and 94 g dm^{-3} Na_2SO_4 at pH 6. The corrosion potential was measured in relation to a mercury sulfate reference electrode (SSE) of potential +0.670 V vs NHE at a room temperature. After 24 h it reached constant value.

The corrosion test was carried out in a salt spray chamber at 25 ± 2 °C, in accordance with the requirements of the Bulgarian State Standards (reg. no. 9227-96). All coatings were 12 μm thick. Some of the coatings were chromated with iridescent yellow chromate [20] for 5 or 20 s. Every 24 h we estimated the samples according to the number and distribution of corrosion defects (flaws, cracks, bubbles, scaling and others) as well as to the appearance of white and red rust.

3. Results and discussion

3.1. *Corrosion potential measurement*

Tables 1 and 2 show the relation between corrosion potential ($E_{corr.}$) and the number, thickness and arrangement of the sublayers for the CMM deposited from a dual bath. Table 1 shows this relation for coatings with an oversublayer of Zn. It is seen that, regardless of the number of sublayers (with equal sublayer thickness) $E_{corr.}$ is much more positive (from −0.905 V to −0.950 V), than that of a pure Zn coating with a thickness of 12 μm (−1.350 V). This means that the CMM have better corrosion resistance in comparison to the pure Zn coating with the same total thickness.

When the CMM consists of eight alternate sublayers (3.0 μm thick sublayers of Co and 0.3 μm thin sublayers of Zn) and the oversublayer is 0.3 μm Zn (see Table 1), $E_{corr.}$ is even more positive (−0.875 V) than $E_{corr.}$ (−0.905 V) of the coatings consisting of four or five sublayers, where the oversublayer is 3.0 μm Zn. When the CMM consists of eight alternate sublayers (0.3 μm thin sublayers of Co and 3.0 μm thick sublayers of Zn) and the oversublayer is 3.0 μm Zn, $E_{corr.}$ (−1.190 V) is significantly more negative than the CMM consisting of eight alternate sublayers described above. Therefore, $E_{corr.}$ of the coatings is determined by the thick (3.0 μm) sublayers of Co or Zn, respectively.

Table 2 shows the same relation for the coatings where the oversublayer is Co. It is seen that, regardless of the number of sublayers (with equal sublayer thickness) $E_{corr.}$ is again much more positive (from −0.885 to −0.950 V) than that of the pure Zn coating and is close to that for the CMM where the oversublayer is Zn (Table 1).

When the CMM consists of eight alternate sublayers (3.0 μm thick sublayers of Zn and 0.3 μm thin sublayers of Co) and the oversublayer is 0.3 μm Co (see Table 2), $E_{corr.}$ (−1.135 V) is more negative than that of the coatings consisting of four or five sublayers, where the oversublayer is 3.0 μm Co (−0.885 and −0.910 V, respectively). This potential is close to $E_{corr.}$ of the CMM consisting of alternate thin (0.3 μm) sublayers of Co and thick (3.0 μm) sublayers of Zn (−1.190 V) (Table 1).

When the CMM consists of eight alternate sublayers (0.3 μm thin sublayers of Zn and 3.0 μm thick sublayers

Table 1. Dependence of corrosion potential ($E_{corr.}$) on type of deposit: Zn–Co CMM electrodeposited from dual bath; Zn oversublayer

Deposit	Number of layers (n)	Number of sublayers ($2n$)	$E_{corr.}$ /V vs SSE
12 μm Zn			−1.350
[3.0 μm Co + 3.0 μm Zn]$_n$	2	4	−0.905
3.0 μm Zn + [3.0 μm Co + 3.0 μm Zn]$_n$	2	5	−0.905
[0.3 μm Co + 0.3 μm Zn]$_n$	20	40	−0.950
0.3 μm Zn + [0.3 μm Co + 0.3 μm Zn]$_n$	24	49	−0.950
[3.0 μm Co + 0.3 μm Zn]$_n$	4	8	−0.875
[0.3 μm Co + 3.0 μm Zn]$_n$	4	8	−1.190

Table 2. Dependence of corrosion potential ($E_{corr.}$) on type of deposit: Zn–Co CMM electrodeposited from dual bath; Co oversublayer

Deposit	Number of layers (n)	Number of sublayers ($2n$)	$E_{corr.}$ /V vs SSE
12 μm Co			−0.650
[3.0 μm Zn + 3.0 μm Co]$_n$	2	4	−0.885
3.0 μm Co + [3.0 μm Zn + 3.0 μm Co]$_n$	2	5	−0.910
[0.3 μm Zn + 0.3 μm Co]$_n$	20	40	−0.940
0.3 μm Co + [0.3 μm Zn + 0.3 μm Co]$_n$	24	49	−0.950
[3.0 μm Zn + 0.3 μm Co]$_n$	4	8	−1.135
[0.3 μm Zn + 3.0 μm Co]$_n$	4	8	−0.855

of Co) and the oversublayer is 3.0 μm Co (see Table 2), $E_{\mathrm{corr.}}$ (-0.855 V) is more positive than that of the CMM where the sublayers are of equal thickness and the oversublayer is Co (from -0.885 to -0.950 V). This potential is close to $E_{\mathrm{corr.}}$ of the coating consisting of alternate thick (3.0 μm) sublayers of Co and thin (0.3 μm) sublayers of Zn where the oversublayer is Zn (-0.875 V) (Table 1). These results confirm the assumption that $E_{\mathrm{corr.}}$ is determined by predominant quantity of the metal Zn or Co in the coatings, respectively.

Tables 3 and 4 show the relation between $E_{\mathrm{corr.}}$ and the number, thickness and arrangement of the sublayers for the CMM deposited from a single bath. Table 3 shows this relation for coatings where the oversublayer is Zn–Co 1% alloy. It is seen that when the sublayers are of equal thickness the increase in the number of sublayers from four to 49 leads to an increase in $E_{\mathrm{corr.}}$ from -0.895 V (four sublayers) to -0.580 V (49 sublayers). Therefore the CMM deposited from single bath also have better corrosion resistance compared to a pure Zn coating of the same total thickness.

When the CMM consists of eight alternate sublayers (0.3 μm thin sublayers of Zn–Co 6.5% alloy and 3.0 μm thick sublayers of Zn–Co 1% alloy) and the oversublayer is Zn–Co 1% (see Table 3), $E_{\mathrm{corr.}}$ (-1.015 V) is significantly more negative compared to $E_{\mathrm{corr.}}$ of coatings consisting of sublayers of equal thickness.

Table 4 shows the same relation for coatings where the oversublayer is Zn–Co 6.5% alloy. It is seen that when the number of sublayers increases from four to 49 (and the sublayers are of equal thickness), $E_{\mathrm{corr.}}$ increases from -0.770 V (four sublayers) to -0.520 V (49 sublayers). Therefore, the CMM have better corrosion resistance than both pure Zn coatings and coatings where the oversublayer is Zn–Co 1% (Table 3).

When the CMM consists of eight alternate sublayers (3.0 μm Zn–Co 1% sublayers and 0.3 μm Zn–Co 6.5% sublayers) where the oversublayer is Zn–Co 6.5% (see Table 4), $E_{\mathrm{corr.}}$ (-1.010 V) is significantly more negative compared to the potentials of the coatings consisting of sublayers of equal thickness and is close to that of alternate thin (0.3 μm) sublayers of Zn–Co 6.5% and thick (3.0 μm) sublayers of Zn–Co 1% (Table 3). The results also confirm the statement that $E_{\mathrm{corr.}}$ is determined by the metal which has predominant quantity (Zn in this case).

The results show that $E_{\mathrm{corr.}}$ of the coatings obtained from a single bath are more positive than those obtained from a dual bath for the same number of sublayers and with the same thickness of the individual sublayer. This can be explained if the CMM is regarded as a system of short-circuited galvanic elements dipped into the electrolyte.

When the CMM consists of sublayers of pure Zn and pure Co the potential difference (ΔE) of the microelements will be:

$$\Delta E = E_{\mathrm{corr.}}^{\mathrm{Co}} - E_{\mathrm{corr.}}^{\mathrm{Zn}} = 0.710\ \mathrm{V}$$

$$E_{\mathrm{corr.}}^{\mathrm{Co}} = -0.640\ \mathrm{V\ vs\ SSE}$$

$$E_{\mathrm{corr.}}^{\mathrm{Zn}} = -1.350\ \mathrm{V\ vs\ SSE}$$

When the CMM consists of alloyed sublayers of different Co content the ΔE of the microelements will be:

$$\Delta E = E_{\mathrm{corr.}}^{\mathrm{Zn\text{–}Co6.5\%}} - E_{\mathrm{corr.}}^{\mathrm{Zn\text{–}Co1\%}} = 0.110\ \mathrm{V}$$

$$E_{\mathrm{corr.}}^{\mathrm{Zn\text{–}Co6.5\%}} = -1.040\ \mathrm{V\ vs\ SSE}$$

$$E_{\mathrm{corr.}}^{\mathrm{Zn\text{–}Co1\%}} = -1.150\ \mathrm{V\ vs\ SSE}$$

Table 3. Dependence of corrosion potential ($E_{\mathrm{corr.}}$) on type of deposit: Zn–Co CMM electrodeposited from single bath; Zn–Co 1% oversublayer

Deposit	Number of layers (n)	Number of sublayers ($2n$)	$E_{\mathrm{corr.}}$ /V vs SSE
12 μm Zn–Co 1%			−1.150
[3.0 μm Zn–Co 6.5% + 3.0 μm Zn–Co 1%]$_n$	2	4	−0.895
3.0 μm Zn–Co 1% + [3.0 μm Zn–Co 6.5% + 3.0 μm Zn–Co 1%]$_n$	2	5	−0.730
[0.3 μm Zn–Co 6.5% + 0.3 μm Zn–Co 1%]$_n$	20	40	−0.640
0.3 μm Zn–Co 1% + [0.3 μm Zn–Co 6.5% + 0.3 μm Zn–Co 1%]$_n$	24	49	−0.580
[0.3 μm Zn–Co 6.5% + 3.0 μm Zn–Co 1%]$_n$	4	8	−1.015

Table 4. Dependence of corrosion potential ($E_{\mathrm{corr.}}$) on type of deposit: Zn–Co CMM electrodeposited from single bath; Zn–Co 6.5% oversublayer

Deposit	Number of layers (n)	Number of sublayers ($2n$)	$E_{\mathrm{corr.}}$ /V vs SSE
12 μm Zn–Co 6.5%			−1.040
[3.0 μm Zn–Co 1% + 3.0 μm Zn–Co 6.5%]$_n$	2	4	−0.770
3.0 μm Zn–Co 6.5% + [3.0 μm Zn–Co 1% + 3.0 μm Zn–Co 6.5%]$_n$	2	5	−0.620
[0.3 μm Zn–Co 1% + 0.3 μm Zn–Co 6.5%]$_n$	20	40	−0.535
0.3 μm Zn–Co 6.5% + [0.3 μm Zn–Co 1% + 0.3 μm Zn–Co 6.5%]$_n$	24	49	−0.520
[3.0 μm Zn–Co 1% + 0.3 μm Zn–Co 6.5%]$_n$	4	8	−1.010

It is seen that the ΔE of the galvanic elements consisting of pure metal sublayers (0.710 V) is many times greater than that of elements consisting of alloyed sublayers (0.110 V), this being attributed to ennobling of the zinc by alloying it with cobalt in the second case. The greater potential difference of the galvanic elements consisting of pure metals (where Zn is anode) results in more active zinc dissolution in the corrosion medium. This is the reason for the more negative corrosion potential of this multilayer system, and for its lower corrosion resistance, respectively, compared to the multilayer system consisting of alloyed sublayers of different amounts of Co.

3.2. *Neutral salt spray (NSS) test*

Tables 5 and 6 show the time to the appearance of white or red rust on the surface of the CMM coatings in dependance on their type (composition, number and arrangement of sublayers). Standard Zn and Zn–Co 0.8% alloyed coatings with a thickness of 12 μm are shown in the Tables for comparison. Table 5 shows the results for the CMM consisting of four sublayers with 3.0 μm individual thickness. After 24 h of salt spray corrosion test, the entire surface of the nonchromated coatings was covered with white rust. The time to the appearance of white rust is the longest for the CMM deposited from a single bath with an oversublayer of Zn–Co 1% and chromated for 20 s. This time is longer (about 100 h) for the coatings deposited from a single bath than that of the coatings deposited from a dual bath. It is seen also that for the CMM with an oversublayer of pure Zn, pure Co or alloy of Zn–Co 1% no red rust appears on the surface even after 1584 h. The CMM deposited from a single bath and non-chromated

Table 5. Time to first appearance of white and red rust in NSS test for pure Zn, Zn–Co 0.8% alloy and Zn–Co CMM consisting of four sublayers with 3.0 μm individual thickness

Deposit	Number of layers (n)	Number of sublayers ($2n$)	Passivation time/s	Time to white rust/h	Time to red rust/h
12 μm Zn			without	24	–
			5	144	504
			20	168	528
12 μm ZnCo 0.8%			without	24	–
			5	288	888
			20	312	960
[3.0 μm Co + 3.0 μm Zn]$_n$	2	4	without	24	–
			5	456	1080
			20	480	1584*
[3.0 μm ZnCo 6.5% + 3.0 μm Zn–Co 1%]$_n$	2	4	without	24	264
			5	552	1584*
			20	576	1584*
[3.0 μm Zn + 3.0 μm Co]$_n$	2	4	without	24	–
			20	360	1584*
[3.0 μm Zn–Co 1% + 3.0 μm Zn–Co 6.5%]$_n$	2	4	without	24	–
			20	192	576

* During the treathment the red rust does not appear

Table 6. Time to first appearance of white and red rust in NSS test for pure Zn, Zn–Co 0.8% alloy and Zn–Co CMM consisting of 40 sublayers with 0.3 μm individual thickness

Deposit	Number of layers (n)	Number of sublayers ($2n$)	Passivation time/s	Time to white rust/h	Time to red rust/h
12 μm Zn			without	24	–
			20	168	528
12 μm Zn–Co 0.8%			without	24	–
			20	312	960
[0.3 μm Co + 0.3 μm Zn]$_n$	20	40	without	24	48
			20	244	1272
[0.3 μm Zn–Co 6.5% + 0.3 μm Zn–Co 1%]$_n$	20	40	without	24	–
			20	96	432
[0.3 μm Zn + 0.3 μm Co]$_n$	20	40	without	24	96
			20	192	576
[0.3 μm Zn–Co 1% + 0.3 μm Zn–Co 6.5%]$_n$	20	40	without	24	48
			20	24	216

have 264 h of salt spray corrosion test to the appearance of red corrosion. These results are in a good agreement with the results obtained from the corrosion potential measurements.

Table 6 shows the same relation but for the CMM consisting of 40 sublayers with 0.3 μm individual thickness. After 24 h of salt spray corrosion test, the entire surface of the nonchromated coatings was covered with white rust. The 20 s iridescent yellow chromating significantly increases their corrosion resistance. The time to the appearance of white rust is shorter for all CMM than that of the coating of Zn–Co 0.8% alloy. This time is longer for the CMM deposited from a dual bath with oversublayers respectively of Zn or Co than that of the pure Zn coating. It is also seen that the time to the appearance of red rust for some of nonchromated CMM is longer than that of the pure Zn and Zn–Co 0.8% alloyed coatings. Multilayer coatings deposited from a dual bath crack into small surface scales after being in the chamber for 2–3 day. Regardless of this, the red rust appears later than in the case of the coatings deposited from a single bath where no cracking is observed.

The data show that the time both to the appearance of white and red rust for the chromated CMM coatings with 0.3 μm individual sublayers thickness at the same total thickness (12 μm) is shorter than the time for the CMM coatings with 3.0 μm individual sublayers thickness. However, the time to the appearance of red rust for the nonchromated CMM coatings with 0.3 μm sublayers thickness is longer compared to that where the thickness of the sublayers is 3.0 μm. The results show that the chromating of CMM consisting of a great number of thin sublayers deteriorates their corrosion resistance compared to those of pure Zn, Zn–Co 0.8% alloy and CMM coatings consisting of four thick (3.0 μm) sublayers.

4. Conclusions

The corrosion potentials of coatings deposited from a single bath are more positive than those of the coatings deposited from a dual bath when the number of the sublayers and their individual thickness are the same. This is attributed to the greater potential difference between pure (Zn and Co) metal galvanic elements when the CMM are deposited from a dual bath.

The best corrosion resistance with regard to the appearance of white rust was observed for the CMM chromated for 20 seconds and consisting of four sublayers, each 3.0 μm thick, deposited from a single bath where the oversublayer is Zn–Co 1%. The corrosion resistance of coatings deposited from a single bath is better than that of the coatings deposited from a dual bath. For CMM with an oversublayer of Zn, Co or Zn–Co 1% no red rust appears 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 is much better than that of pure Zn or Zn–Co 0.8% alloyed coatings.

The chromated CMM consisting of 40 sublayers with 0.3 μm individual thickness are less corrosion resistant than the CMM with 3.0 μm sublayers thickness. The nonchromated CMM with 0.3 μm sublayers thickness have better corrosion resistance with regard to the appearance of red rust compared to that of pure Zn or Zn–Co 0.8% alloyed coatings. The iridescent yellow chromating of the CMM consisting of a great number of thin sublayers deteriorates their corrosion resistance.

Acknowledgement

The authors are grateful to the National Foundation ‘Scientific Investigations’, Bulgaria for the obtained financial assistance.

References

1. M. Kalantary, G. Wilcox and D. Gabe, *Electrochim. Acta* **40** (1995) 1609.
2. G. Barral and S. Maximovich, *Colloq. Phys., Colloque C4* **51** (1990) 291.
3. D. Simunovich and M. Schlesinger, *J. Electrochem. Soc.* **141** (1994) L10.
4. J. Celis, A. Haseeb and J. Roos, *Trans. Inst. Metal. Finish.* **70** (1992) 123.
5. A. Haseeb, J. Celis and J. Roos, *J. Electrochem. Soc.* **141** (1994) 230.
6. C.-C. Yang and H. Cheh, *J. Electrochem. Soc.* **142** (1995) 3034.
7. C.-C. Yang and H. Cheh, *J. Electrochem. Soc.* **142** (1995) 3040.
8. A. Stankeviciute, K. Leinartas, G. Bikulcius, D. Virbaye, A. Sudavicius and E. Juzeliunas, *J. Appl. Electrochem.* **28** (1998) 89.
9. N. Short, A. Abibsi and J. Dennis, *Trans. Inst. Metal. Finish.* **67** (1989) 73.
10. G. Loar, K. Romer and T. Aoe, *Plat. Surf. Finish.* **78** (1991) 74.
11. M. Kalantary, *Plat. Surf. Finish.* **81** (1994) 80.
12. D. Crotty and R. Griffin, *Plat. Surf. Finish.* **86** (1997) 57.
13. I. Kirilova and I. Ivanov, *J. Appl. Electrochem.* **28** (1998) 1359.
14. I. Kirilova and I. Ivanov, *Bul. Chem. Commun.* **29**(2) (1996/97) 355.
15. I. Kirilova and I. Ivanov, *Bul. Chem. Commun.* **29**(2) (1996/97) 204.
16. I. Kirilova and I. Ivanov, *J. Appl. Electrochem.* **27** (1997) 1380.
17. I. Kirilova and I. Ivanov, *J. Appl. Electrochem.* **28** (1998) 637.
18. *Bulg. Patent 39 402* (1978).
19. *SU Patent. 1813808A1* (1990).
20. *Bulg. Patent. 29 959* (1981).