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Anodic behaviour of one and two-layer coatings of Zn and Co electrodeposited from single and dual baths

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One and two-layer Zn and Co coatings deposited from single and dual baths have been studied. During potentiodynamic stripping of a two-layer coating deposited from dual baths, containing either Zn^{2+} or Co^{2+}, composed of a Co underlayer and a Zn overlayer, two separate peaks are observed, corresponding to the dissolution of both metals independently of one another. When the overlayer is of Co, the predominant part of the two-layer coating is stripped at the dissolution potential of pure Co coatings. In the anodic dissolution curve of a two-layer coating deposited from a single bath, containing both Zn^{2+} and Co^{2+}, composed of a Zn layer with low (1.0%) Co content and a layer with high (6.5%) Co content, three anodic current peaks are observed. These are due to the dissolution of pure Zn and of Zn–Co alloy phases. The heights of the peaks and the potentials of their maxima do not depend on the order of layers but only on their thickness.

Keywords: *Zn–Co alloy*, *multilayers*, *stripping method*, *corrosion resistance*

1. Introduction

Electrodeposits consisting of a large number of very thin metal or alloy layers, named composition-modulated multilayers (CMM), possess improved properties such as increased corrosion resistance, microhardness, mechanical strength etc. However, literature information, concerning the deposition of such CMM systems consisting of pure Zn and Co or of their alloys, is absent.

Electrochemical stripping methods have been proposed to characterize the alloy deposition process and product [1–15]. Stripping studies are an accelerated corrosion test of the deposits and provide information about the preferential corrosion of the less noble component. When an alloy is polarized anodically under potentiodynamic conditions, the components are dissolved at various potentials, which gives rise to various peaks. The peak structure is characteristic of the alloy components and the phase structure of the deposit. A binary alloy with no miscibility (solubility) between components in the solid phase (eutectic type) is characterized by two sharp dissolution peaks. In alloys with complete miscibility between the components in the solid phase (solid solution) the latter are dissolved simultaneously. In the case of alloys with the formation of intermediate phases and/or intermetallic compounds, each phase or compound displays its own dissolution peak.

The aim of the present work is to obtain, by means of the potentiodynamic stripping, indirect data about the phase composition and electrochemical behaviour of one and two-layer coatings, electrodeposited from baths containing either one of the ions or both Zn^{2+} and Co^{2+}. This study is the first of a series of papers dedicated to Zn–Co CMM from single and dual baths.

2. Experimental details

All experiments were carried out in a conventional electrochemical glass cell. The cathode was a $1.0\,cm^2$ copper plate and both anodes were $2.0\,cm^2$ platinum plates. Before electrolysis the cathode surface was polished with emery paper (grit 600) and was etched in 1 : 1 HNO_3. The cathodic potential was measured against a mercury sulfate reference electrode (SSE), with potential $+0.670$ V vs NHE. The temperature of the electrolytes was 25 ± 1 °C and was kept constant using an UH-16 thermostat.

One and two-layer coatings were deposited galvanostatically using a TEC 88 galvanostat and the current was measured with an ML-10 ammeter. The potentiodynamic stripping was carried out in the zinc electrolyte without additives. The coatings obtained were studied at a scanning rate $1\,mV\,s^{-1}$ using a potentiostat (Elpan, EP 20A) and a scanner (Elpan, EG 20). The current–voltage dependence (stripping voltammogram) was recorded with an X–Y plotter (Endim 622.01). The amount of deposited metal was presented (in coulombs) by the charge associated with the stripping peaks. The potential was checked with a (V-542.1) digital voltmeter (Meratronik, Poland).

The coatings from dual baths were deposited from the following electrolytes. The zinc electrolyte contained $175\,g\,dm^{-3}$ $ZnSO_4.7H_2O$, $22\,g\,dm^{-3}$ $(NH_4)_2SO_4$,

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† Deceased.

30 g dm^{-3} H_3BO_3 and the commercial additives AZ-1 (50 cm^3 dm^{-3}) and AZ-2 (10 cm^3 dm^{-3}). The AZ-1 additive was 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 3–30) and of the sodium or potassium salt of benzoic acid and AZ-2 brightening additive was composed of benzylidene acetone ($C_6H_5CHO{=}CHC_2H_5$) and ethanol [16]. The pH of the bath was 4.5. 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, saccharin (2 g dm^{-3}), the brightening additive hydroxyethylated-buthyn-2-diol-1,4 ($HOCH_2{\equiv}CCH_2OCH_2CH_2OH$) (EAA) at 5 cm^3 dm^{-3} (30% solution), and the antipitting additive Na-decylsulfate (EFAP) at 2 mg dm^{-3}. The pH of the bath was 2.5.

The coatings from a single bath were deposited 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, AZ-1 (50 cm^3 dm^{-3}), AZ-2 (10 cm^3 dm^{-3}), saccharin (2 g dm^{-3}, EFAP (2 mg dm^{-3}), and 5 cm^3 dm^{-3} 30% solution of EAA. The pH of the bath was 2.5.

3. Results and discussion

3.1. *One and two-layer coatings deposited from dual baths containing either zinc or cobalt ions*

All coatings were deposited at a current density of 2 A dm^{-2}. Coatings 0.3 μm thick were deposited for 1 min (Co coatings) and for 35 s (Zn coatings). Coatings 3.0 μm thick were deposited for 8 min (Co coatings) and for 5 min (Zn coatings). The two-layer coatings were obtained by subsequent manual transfer of the substrate from the first to the second bath, with rinsing between the deposition of the first and the second layer.

3.1.1. Coatings with a zinc overlayer. Figure 1, curve 1 shows the voltammogram for potentiodynamic stripping of a 0.3 μm thick Zn layer. Two stripping peaks are observed at potentials −1.240 V and −1.300 V. Initially a larger amount of Zn dissolves, which displays a peak at −1.300 V during potentiodynamic stripping. A small amount of Zn, more strongly bound to the copper substrate, dissolves at more positive potential, which gives a peak at −1.240 V. When a thicker (3.0 μm) Zn coating is stripped (curve 2), only one peak at −1.180 V is observed. Curve 3 shows a voltammogram for dissolution of a coating containing a Co layer (0.3 μm) and a Zn overlayer (0.3 μm). Two double peaks are seen in the curve. The peak with two maxima at −1.260 V and −1.290 V is due to the complete dissolution of the Zn overlayer. The peak with two maxima at −0.560 V and −0.630 V is due to Co dissolution. Curve 4 shows the same dependence for stripping of a coating composed of 3.0 μm Co and 3.0 μm Zn. Two single peaks on the curve, which are due to the dissolution of Zn (at −1.170 V) and of Co (at −0.540 V) are observed.

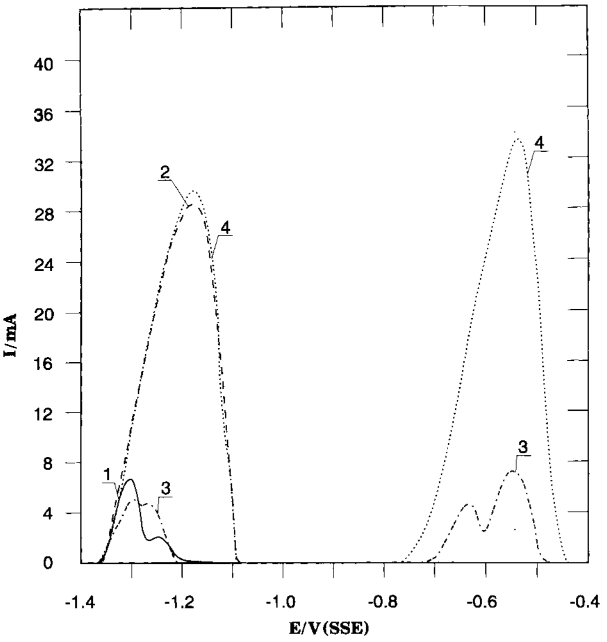

Fig. 1. Stripping voltammograms of coatings deposited in dual baths: (1) 0.3 μm Zn; (2) 3.0 μm Zn; (3) 0.3 μm Co + 0.3 μm Zn; (4) 3.0 μm Co + 3.0 μm Zn.

Figure 2 shows the stripping voltammogram when the first Co layer is 3.0 μm thick and the second Zn overlayer is 0.3 μm (curve 1) and when the first Co layer is 3.0 μm and the second Zn overlayer is 3.0 μm (curve 2). These dependencies are similar to those shown in Fig. 1. The absence of the zinc peak at −1.240 V (curve 1) (which is seen in Fig. 1, curve 1) is probably due to the influence of the thick (3.0 μm) Co layer.

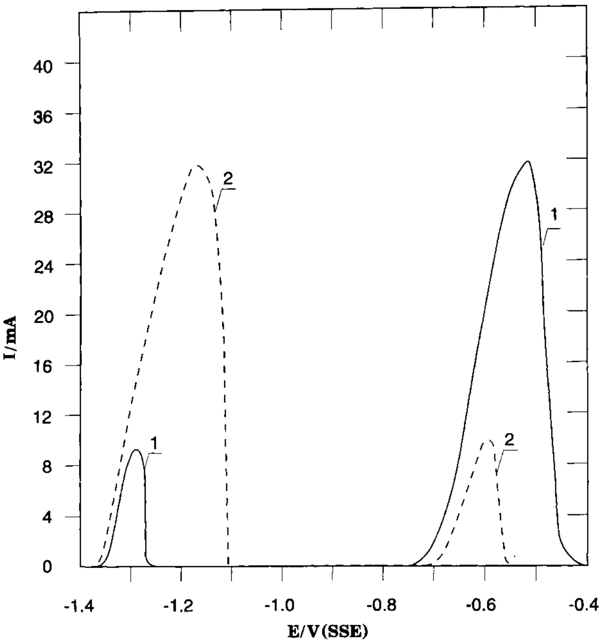

Fig. 2. Stripping voltammograms of coatings deposited in dual baths: (1) 3.0 μm Co + 0.3 μm Zn; (2) 0.3 μm Co + 3.0 μm Zn.

Table 1. Dependence of potential of the stripping peak maximum, amount of dissolved metal (in coulombs) and its relation to the amount of the dissolved entire deposit (in %) on the deposit type

Coatings were deposited from dual baths

Deposit	*Peak (I)*			*Peak (II)*		
	E_A^{peakI} /V vs SSE	q^I/C	$\frac{q^I}{q^I+q^{II}}\Big/\%$	E_A^{peakII} /V vs SSE	q^{II}/C	$\frac{q^{II}}{q^I+q^{II}}\Big/\%$
0.3 μm Zn				−1.240∼−1.300	0.5	100.0
3.0 μm Zn				−1.180	4.5	100.0
0.3 μm Co + 0.3 μm Zn	−0.560∼−0.630	0.8	59.0	−1.260∼−1.290	0.5	41.0
3.0 μm Co + 3.0 μm Zn	−0.540	4.5	52.0	−1.170	4.1	48.0
3.0 μm Co + 0.3 μm Zn	−0.525	4.3	90.1	−1.290	0.5	9.9
0.3 μm Co + 3.0 μm Zn	−0.610	0.7	13.0	−1.170	4.6	87.0

The curves in Fig. 1 and Fig. 2 show that the two metal layers, the upper one being Zn, dissolve consecutively and independently of one another at potentials typical for the Zn and Co monolayers of the same thickness. The results obtained are presented also in Table 1.

3.1.2. Coatings with a cobalt overlayer. Figure 3, curve 1 shows the stripping voltammogram when a Co coating 0.3 μm thick dissolves. A peak at −0.640 V is observed with an inflexion point at −0.625 V, which is due to Co dissolution. When a 3.0 μm thick Co coating is stripped a larger peak at potential −0.525 V appears (curve 2). When a double-layer coating composed of Zn (0.3 μm) and Co (0.3 μm) layers is stripped, a very small peak at −1.275 V appears on the voltammogram (curve 3) which is due to the dissolution of only 5.0% of the Zn coating and a higher peak appears at −0.625 V (1.0 C), due to the dissolution of the remaining 95.0% of the deposited Zn and the total amount of the deposited Co. When a two-layer coating composed of Zn (3.0 μm) and Co (3.0 μm) layers is stripped (curve 4) then at −1.220 V only 31.2% (2.8 C) of the whole coating is dissolved (which is 60% of the deposited Zn) and at −0.540 V the remaining Zn and total of Co (i.e. 68.8%) of the coating (6.1 C) is dissolved. In this case the protective effect of the Co overlayer is less than in the previous case. Probably this is due to a higher porosity of the thicker Co overlayer.

Figure 4 shows the stripping curves of a two-layer coating, composed of a Zn layer (3.0 μm) and a 0.3 μm Co overlayer (curve 1) and of a two-layer coating composed of a (0.3 μm) Zn layer and a (3.0 μm) Co overlayer (curve 2). It is seen that when the thick (3.0 μm) Zn layer is covered with a thin (0.3 μm) Co overlayer, at potentials −1.125 V and −1.250 V more than half of the coating is dissolved (52.2%). This means that the thin Co overlayer does not completely protect the thick Zn underlayer. In the case when the thin (0.3 μm) Zn layer is covered with a thick (3.0 μm) Co overlayer, the entire coating is dissolved at a potential of −0.560 V, which is typical

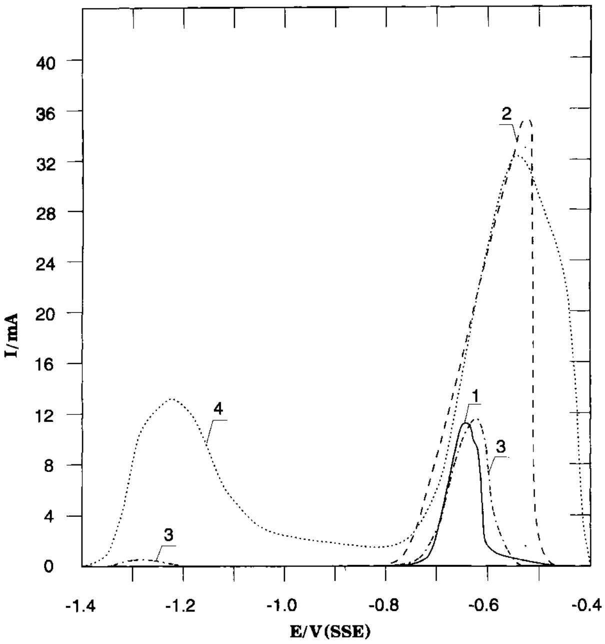

Fig. 3. Stripping voltammograms of coatings deposited in dual baths: (1) 0.3 μm Co; (2) 3.0 μm Co; (3) 0.3 μm Zn + 0.3 μm Co; (4) 3.0 μm Zn + 3.0 μm Co.

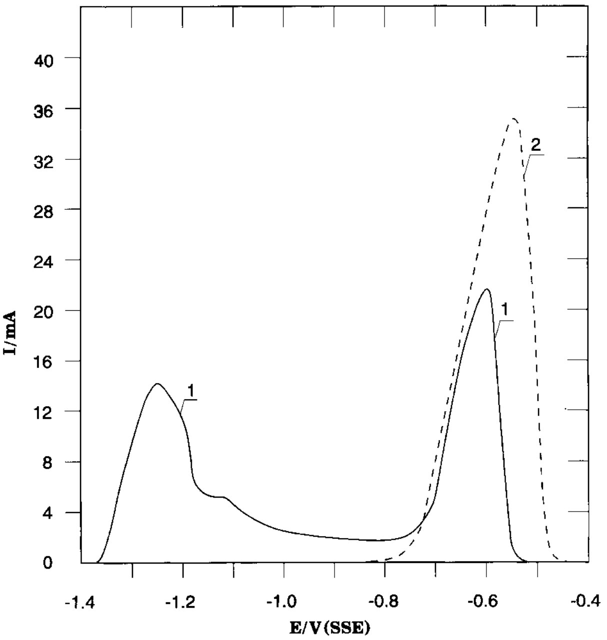

Fig. 4. Stripping voltammograms of coatings deposited in dual baths: (1) 3.0 μm Zn + 0.3 μm Co; (2) 0.3 μm Zn + 3.0 μm Co.

Table 2. Dependence of potential of the stripping peak maximum, amount of the dissolved metal (in coulombs) and its relation to the amount of the dissolved entire deposit (in %) on the deposit type

Coatings were deposited from dual baths

Deposit	*Peak (I)*			*Peak (II)*		
	E_A^{peakI}/V vs SSE	q^I/C	$\frac{q^I}{q^I+q^{II}}\Big/\%$	E_A^{peakII} / V vs SSE	q^{II}/C	$\frac{q^{II}}{q^I+q^{II}}\Big/\%$
0.3 μm Co	−0.625* ~ −0.640	0.7	100.0			
3.0 μm Co	−0.525	4.4	100.0			
0.3 μm Zn + 0.3 μm Co	−0.625	1.0	95.0	−1.275	0.1	5.0
3.0 μm Zn + 3.0 μm Co	−0.540	6.1	68.8	−1.220	2.8	31.2
3.0 μm Zn + 0.3 μm Co	−0.610	2.2	47.8	−1.125 ~ −1.250	2.4	52.2
0.3 μm Zn + 3.0 μm Co	−0.560	4.8	100.0			

* inflexion point

for the dissolution of 3.0 μm pure Co. This means that during potentiodynamic stripping the thick Co overlayer completely protects the thin Zn underlayer. These results are also shown in Table 2.

3.2. *One and two-layer coatings deposited from single bath containing both zinc and cobalt ions*

It has been stated elsewhere [17] that the most homogeneous, smooth, dense and bright (or semibright) Zn–Co coatings (with good adhesion to the substrate) are deposited from an electrolyte containing 1 M Co^{2+} and 0.6 M Zn^{2+}. At a current density of 0.2 A dm^{-2}, a Zn–Co alloy coating containing 1.0% Co was deposited; at 2 A dm^{-2} a Zn–Co alloy with 6.5% Co. The two-layer coatings were obtained by stepping up the current density. The 0.3 μm thick Zn–Co(1%) coatings were deposited for 7 min, and 0.3 μm Zn–Co(6.5%) for 45 s. The 3.0 μm thick Zn–Co(1%) coatings were deposited for 1 h, and the 3.0 μm Zn–Co(6.5%) for 7 min.

3.2.1. Coatings, finishing with a Zn–Co alloy with low (1%) Co content. Figure 5, curve 1 shows the voltammogram for potentiodynamic stripping of a 0.3 μm Zn–Co(1%) coating. A single current peak at −1.310 V occurs, which coincides with a Zn peak (at −1.300 V) obtained when a coating deposited from an electrolyte containing only Zn^{2+} (Fig. 1, curve 1) is stripped. Due to the low Co content in the alloy, a stripping peak due to Co dissolution is not observed. When a thick (3.0 μm) Zn–Co(6.5%) coating is deposited (curve 2) only one stripping peak appears at −1.150 V. Curve 3 shows the stripping voltammogram of a two-layer coating, consisting of a Zn–Co(6.5%) onto which a Zn–Co(1%) layer was deposited. Both layers were 0.3 μm thick. On the stripping curve a larger peak at −1.290 V appears with an inflexion at −1.230 V and a much smaller and ill-defined peak at −1.140 V. The larger peak is probably due to the dissolution of the Zn component, while the smaller one is due to the dissolution of the Zn–Co alloy component in the coating. The fact that this peak appears at a considerably more negative potential (−1.140 V) compared to the peak when pure Co dissolves (−0.640 V) indicates that Co in the coating is probably not in a free state. When the double-layer coating, composed of the same layers, but each 3.0 μm thick is stripped, the stripping peaks merge and form a single large peak at −1.030 V (curve 4). This shift in the positive direction is due to the increase in the quantity of the Zn–Co alloy component, which is dissolved at more positive potentials than that of pure Zn but more negative than that of pure Co.

When coatings composed of a 3.0 μm Zn–Co(6.5%) layer and 0.3 μm Zn–Co(1%) layer is stripped (Fig. 6, curve 1), the stripping curve contains the same peaks as for a 3.0 μm thick coating of Zn–Co(6.5%) (Fig. 7, curve 2). The stripping of a two-layer coating, containing a thin (0.3 μm) Zn–Co(6.5%) layer and a thick (3.0 μm) Zn–Co(1%) layer (Fig. 6, curve 2) displays a large peak at −1.100 V, corresponding to the peak at which a

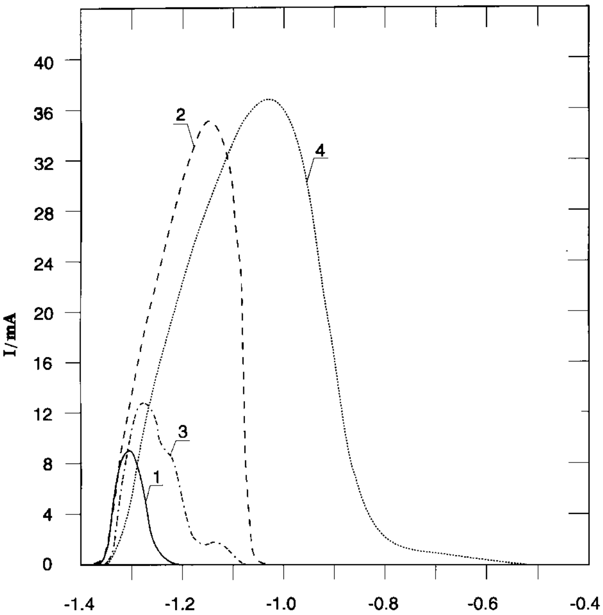

Fig. 5. Stripping voltammograms of coatings deposited in a single bath: (1) 0.3 μm Zn–Co(1%); (2) 3.0 μm Zn–Co(1%); (3) 0.3 μm Zn–Co(6.5%) + 0.3 μm Zn–Co(1%); (4) 3.0 μm Zn–Co(6.5%) + 3.0 μm Zn–Co(1%).

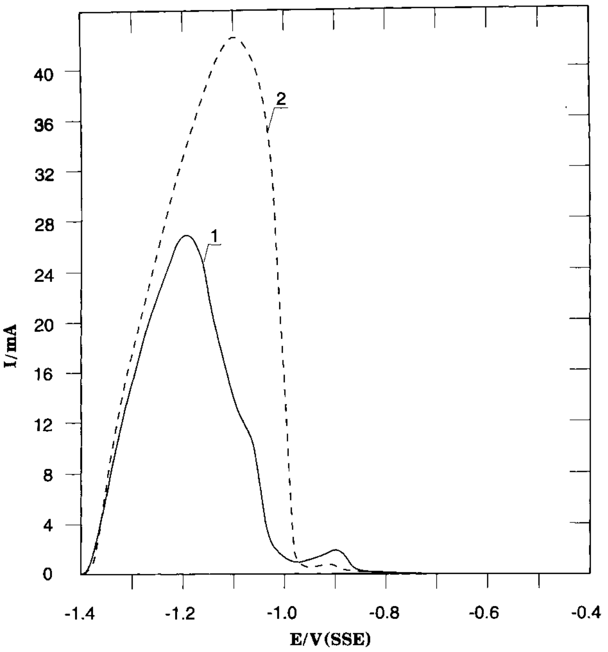

Fig. 6. Stripping voltammograms of coatings deposited in a single bath: (1) 3.0 μm Zn–Co(6.5%) + 0.3 μm Zn–Co(1%); (2) 0.3 μm Zn–Co(6.5%) + 3.0 μm Zn–Co(1%).

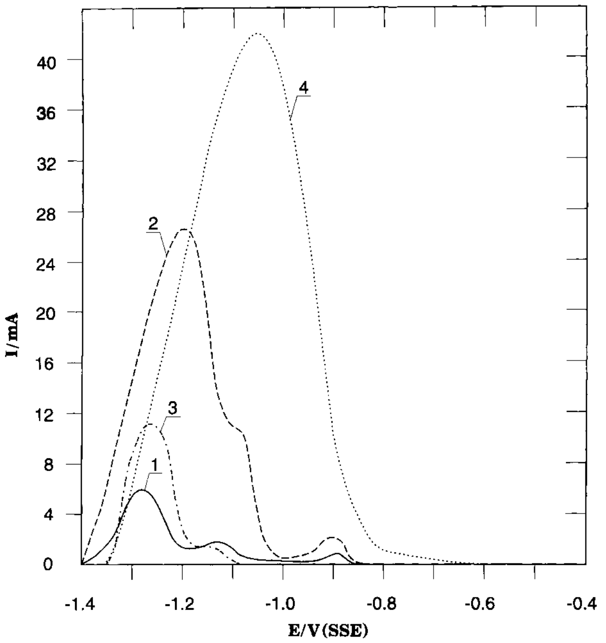

Fig. 7. Stripping voltammograms of coatings deposited in a single bath: (1) 0.3 μm Zn–Co(6.5%); (2) 3.0 μm Zn–Co(6.5%); (3) 0.3 μm Zn–Co(1%) + 0.3 μm Zn–Co(6.5%); (4) 3.0 μm Zn–Co(1%) + 3.0 μm Zn–Co(6.5%).

monolayer (3.0 μm) of Zn–Co(1%) is dissolved (Fig. 5, curve 2) and a much smaller peak at −0.900 V, typical of the dissolution of a Zn–Co(6.5%) layer (Fig. 7, curve 2). The results obtained are presented in Table 3.

3.2.2. Coatings, finishing with a Zn–Co alloy with high (6.5%) Co content. Figure 7, curve 1 shows the voltammogram for potentiodynamic stripping of a 0.3 μm thick Zn–Co(6.5%) coating. Three peaks are evident. The largest at −1.280 V is due to the dissolution of the Zn component, the other two (at −1.125 and −0.900 V) are probably a result of the dissolution of Zn–Co alloys with different composition. Curve 2 shows the stripping of a 3.0 μm Zn–Co(6.5%) coating. In this case two well definited peaks at −0.900 and −1.200 V are observed. The middle peak (observed in Fig. 7, curve 1) is transformed into an inflexion point at −1.075 V as a result of the increase in the Zn peak at −1.200 V. The studies performed indicate that with increase in the Co content (from 1.0 to 6.5%) formation of a new alloy phase begins which dissolves at more positive potentials than that of the pure Zn and displays a current peak shifted towards the potential at which Co is dissolved. Curves 3 and 4 of Fig. 7 show the stripping of two-layer coatings composed of a Zn–Co(1%) layer onto which a Zn–Co(6.5%) overlayer is deposited. When both layers are 0.3 μm thick, two peaks appear in the stripping curve (curve 3), a considerably larger one at −1.260 V (due to Zn dissolution) and a much smaller one at −1.140 V (due to the dissolution of the Zn–Co alloy phase). When both layers are 3.0 μm thick, a large peak at −1.050 V appears (curve 4) as a result of the initial dissolution of pure Zn and the subsequent dissolution of the Zn–Co alloy. The increase in the quantity of deposited metal causes a merger of both peaks and the increase in the relative share of the alloy phase leads to a shift of the peak towards more positive potentials.

In the stripping of both the two-layer coatings (composed of a 3.0 μm Zn–Co(1%) layer and a 0.3 μm Zn–Co(6.5%) overlayer (Fig. 8, curve 1), and of a 0.3 μm Zn–Co(1%) and a 3.0 μm Zn–Co(6.5%)

Table 3. Dependence between the potential of the stripping peak maximum and the deposit type

Coatings are deposited from a single bath

Deposit	$E_A^{peak(i)}$ /V vs SSE			
0.3 μm Zn–Co(1%)				−1.310
3.0 μm Zn–Co(1%)		−1.150		
0.3 μm Zn–Co(6.5%) + 0.3 μm Zn–Co(1%)		−1.140	−1.230*	−1.290
3.0 μm Zn–Co(6.5%) + 3.0 μm Zn–Co(1%)		−1.030		
3.0 μm Zn–Co(6.5%) + 0.3 μm Zn–Co(1%)	−0.900	−1.075*	−1.200	
0.3 μm Zn–Co(6.5%) + 3.0 μm Zn–Co(1%)	−0.900	−1.100		

* inflexion point

Table 4. Dependence between the potential of the stripping peak maximum and the deposit type

Coatings are deposited from a single bath

Deposit	$E_A^{peak(i)}$ /V vs SSE		
0.3 μm Zn–Co(6.5%)	−0.900	−1.125	
3.0 μm Zn–Co(6.5%)	−0.900	−1.075*	−1.200
0.3 μm Zn–Co(1%) + 0.3 μm Zn–Co(6.5%)		−1.140	−1.260
3.0 μm Zn–Co(1%) + 3.0 μm Zn–Co(6.5%)		−1.050	
3.0 μm Zn–Co(1%) + 0.3 μm Zn–Co(6.5%)	−0.940		−1.160
0.3 μm Zn–Co(1%) + 3.0 μm Zn–Co(6.5%)	−0.900	−1.070*	−1.175

* inflexion point

(Fig. 8, curve 2)) two peaks appear: one much higher at −1.160 V (curve 1) and −1.175 V (curve 2), typical of the dissolution of the zinc coating with low Co content, and the other, a very small one, at −0.900 V (curve 1) and −0.940 V (curve 2), typical of the dissolution of a cobalt enriched alloy phase. The results are similar to the dissolution of the single layers 3.0 μm thick (Fig. 5, curve 2 and Fig. 7, curve 2). In all cases the shape of the stripping curves does not depend on the order of the layers. These results are also presented in Table 4.

According to Jović *et al.* [3], the detection of multiple peaks for the dissolution of the deposit can be attributed to the dissolution of metals from different intermediate phases or intermetallic compounds. Therefore, the potentiodynamic response displays various peaks and the peak structure is characteristic of the alloy components and the phase structure of the deposits. The different peaks were assigned to different alloy phases in accordance with the experimental results and the information obtained by phase diagrams and by comparison with related studies of the same or similar alloys [2, 18].

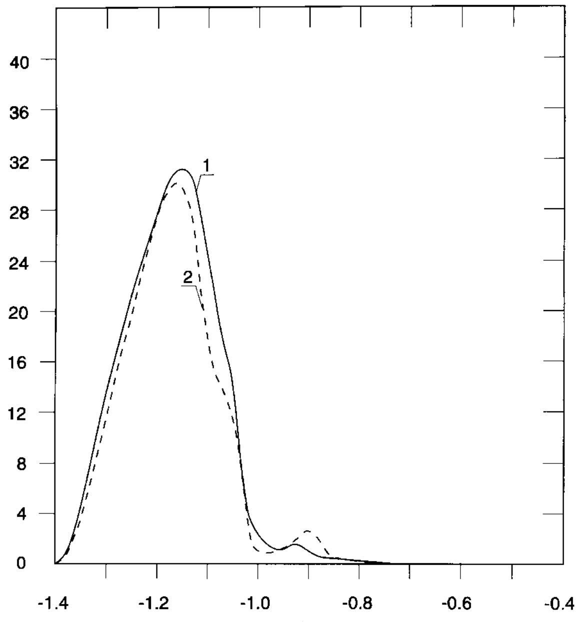

Fig. 8. Stripping voltammograms of coatings deposited in a single bath: (1) 3.0 μm Zn–Co(1%) + 0.3 μm Zn–Co(6.5%); (2) 0.3 μm Zn–Co(1%) + 3.0 μm Zn–Co(6.5%).

Some authors [18–20] have proposed the existence of various Zn-rich phases in Zn–Co alloys: γ_2 (91.0–92.8% Zn), γ_1 (87.4–88.6% Zn) and γ (75.2–85.4% Zn), and a β phase with a slightly higher percentage of Zn (53.0–53.8% Zn). Moreover, the existence of a solid solution with very low Co content ($<$ 1%) has also been proposed (α phase). The stripping peaks were assigned to the different alloy phases by comparing their charges with the microanalysis results of the corresponding deposit [21].

In spite of the absence of experimental evidence, it is obvious that the appearance of such multiple peaks in the curves, is a result of the dissolution of Zn and Co from different intermediate phases or intermetallic compounds.

4. Conclusions

During the potentiodynamic stripping of a two-layer coating deposited from dual baths, containing either Zn^{2+} and Co^{2+}, composed of a Co underlayer and a Zn overlayer, two separate peaks are observed. These correspond to the independent dissolution of both metals. When the overlayer is of Co, most of the two-layer coating is stripped at the potential of pure Co dissolution.

In the anodic dissolution of the two-layer coating obtained from a single bath, containing both Zn^{2+} and Co^{2+}, composed of a Zn–Co(1%) and Zn–Co(6.5%) three anodic current peaks are observed. These are due to the dissolution of pure Zn and of Zn–Co alloy phases. The peak heights and the potentials of their maxima do not depend on the order of the layers but only on their thickness.

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