JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 1359–1363

Anodic behaviour of composition modulated Zn–Co multilayers electrodeposited from single and dual baths

I. KIRILOVA, I. IVANOV, St. RASHKOV[†]

Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Received 18 December 1996; accepted in revised form 20 August 1997

The anodic behaviour of composition modulated Zn–Co multilayers (CMM) electrodeposited from single and dual baths was studied. Multilayers with thickness of the individual sublayers 0.3 and 3.0 μm were electrodeposited galvanostatically. It was established that most of the CMM coatings obtained from dual baths dissolve at potentials that are 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 with equal total thickness, deposited both from dual or single baths, regardless of their individual sublayer thickness and sequence, potentials of the stripping peaks are shifted positively.

Keywords: *cobalt*, *modulated multilayers*, *multilayer deposition*, *zinc*

1. Introduction

New materials called composition modulated multilayers (CMM) are a recent development. Such materials consist of alternate layers, each composed of two sublayers of different metals or alloys. Some multilayer coatings have improved physicomechanical and electrochemical properties compared to traditional alloys. Recently, the number of papers on the formation of different CMM coatings using electrochemical methods has increased: Cu–Ni [1–16], Cu–Fe [17], Cu–Ag [18], brass [19], Zn–Ni [20, 21], Ni–NiP [22, 23], NiP–Sn [24, 25]. Literature data concerning the deposition and properties of CMM systems consisting of pure Zn and Co or their alloys are, however, absent.

2. Experimental details

The experiments were carried out in a conventional electrochemical glass cell. The cathode was a 1.0 cm^2 area Cu plate, and both anodes were 2.0 cm^2 area Pt plates. The cathodic potential was measured relative to a mercury sulphate reference electrode (SSE) of potential +0.670 V vs NHE. The temperature of the electrolytes was (25 ± 1) °C and was kept constant with a UH 16 thermostat.

Composition modulated Zn–Co multilayers were obtained galvanostatically using a TEC 88 galvanostat. The potentiodynamic stripping was carried out in the zinc electrolyte without additives at a scan rate of 1 mV s^{-1} using a potentiostat (EP 20A Elpan) and scanner (EG 20 Elpan). CMM coatings were stripped within the range −1.400 to −0.300 V because at more positive potentials the Cu substrate dissolves. The current–potential dependence (stripping voltammogram) was recorded on a 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 detected with a digital voltmeter V 542.1. The coating composition was determined by X-ray microanalysis using a Super Probe 733 Jeol electron microscope.

CMM 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} $(NH_4)_2SO_4$, 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 alkyl or alkylaryl radical with 1 to 20 carbon atoms in the alkyl group and n is from 3 to 30) and of a sodium or potassium salt of benzoic acid. The AZ-2 brightening additive was composed of benzylidene acetone and ethanol [26]. 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}), brightening additive hydroxyethylated buthyn-2-diol-1,4 ($HOCH_2C{\equiv}CCH_2OCH_2CH_2OH$) (EAA) – 5 cm^3 dm^{-3} (30% solution), and the antipitting additive Na-decylsulphate (EFAP) – 2 mg dm^{-3}. The pH of the bath was 2.5.

CMM 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.

[†] Dr Rashkov passed away in 1996.

0021-891X

3. Results and discussion

3.1. *Multilayer coatings deposited from dual baths containing either zinc or cobalt ions*

All coatings were deposited at a current density of $2\,A\,dm^{-2}$. Sublayers $0.3\,\mu m$ thick were deposited for 1 min (Co sublayers) and for 35 s (Zn sublayers). Sublayers $3.0\,\mu m$ thick were deposited for 8 min (Co sublayers) and for 5 min (Zn sublayers).

Figure 1 shows voltammograms for potentiodynamic stripping of coatings consisting of five sublayers of Co and Zn, each $0.3\,\mu m$ (curves 1 and 2) or $3.0\,\mu m$ (curves 3 and 4) thick. Curves 1 and 3 show the current–potential dependence when the multilayer coating ends with the zinc oversublayer, and curves 2 and 4 when the multilayer coating ends with a cobalt oversublayer. Two stripping peaks appear, the one at the more positive potential is significantly larger in area, that is, the larger part of the multilayer coating dissolves at this potential. Similar behaviour was observed for coatings consisting of 4, 40 and 49 sublayers with equal sublayer thickness as well as for coatings consisting of alternating thin ($0.3\,\mu m$) and thick ($3.0\,\mu m$) sublayers (Tables 1 and 2).

Table 1 presents the relationship between the potential of the stripping peaks against deposit type and against the number of sublayers, when the CMM ends with a zinc oversublayer. Coatings composed of an even number of sublayers begin with cobalt and end with a zinc sublayer. Coatings composed of an odd number of sublayers begin and end with a zinc sublayer.

During the stripping of a deposit composed of four or five $0.3\,\mu m$ thick sublayers at more negative potentials (−1.280 and −1.260 V) a smaller part of the coating (27.9% and 31.0%) dissolves. At these potentials the zinc oversublayer and a part of the zinc sublayers beneath it dissolve. The dissolution of zinc sublayers is more pronounced when the nearest sublayer to the copper substrate (first sublayer) is of zinc (five sublayers). The remaining larger part of the coating strips at more positive potentials (between −0.540 and −0.620 V). In this case, also after the dissolution of the Zn oversublayer, the cobalt sublayer under it protects the rest of zinc sublayers and they strip together with the cobalt sublayers at a substantially more positive potential. Similar behaviour was observed during the stripping of coatings composed of 40 or 49 sublayers $0.3\,\mu m$ thick and of four or five sublayers $3.0\,\mu m$ thick. When the coating is composed of four thick ($3.0\,\mu m$) cobalt and four thin ($0.3\,\mu m$) zinc sublayers the zinc oversublayer and a small part of the other Zn sublayers (3.7%) are dissolved at more negative (−1.300 V) potentials. Thick cobalt sublayers protect the other thin zinc sublayers well, and they dissolve together with the

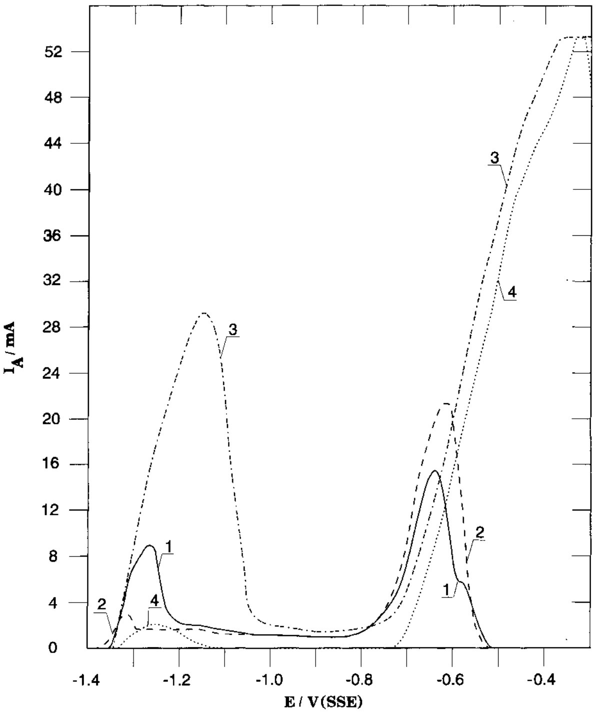

Fig. 1. Stripping voltammograms of Zn–Co coatings consisting of five sublayers deposited from dual baths, each of thickness $0.3\,\mu m$ (1,2) or $3.0\,\mu m$ (3,4): (1) coating ends with a Zn oversublayer; (2) coating ends with a Co oversublayer; (3) coating ends with a Zn oversublayer; (4) coating ends with a Co oversublayer.

Table 1. Characteristic features of different type of deposits, number of layers, potentials of the stripping peak maximums and the ratio (in %) between the area of the individual stripping peaks (q^I, q^{II}) and the total area of both peaks ($q^I + q^{II}$)

The Zn–Co CMM are deposited from dual baths. The oversublayer is of Zn

Deposit	*Number of layers* (*n*)	*Number of sublayers* (*2n*)	*Peak (I)*		*Peak (II)*	
			E_A^{peakI} /V vs SSE	$\frac{q^I}{q^I+q^{II}}$ /%	E_A^{peakII} /V vs SSE	$\frac{q^{II}}{q^I+q^{II}}$ /%
$(0.3\,\mu m$ Co + $0.3\,\mu m$ Zn$)_n$	2	4	−0.550, −0.620	72.1	−1.280	27.9
	20	40	−0.350	98.8	−1.240	1.2
$0.3\,\mu m$ Zn + $(0.3\,\mu m$ Co + $0.3\,\mu m$ Zn$)_n$	2	5	−0.540, −0.610	69.0	−1.260	31.0
	24	49	−0.350	87.1	−1.200	12.9
$(3.0\,\mu m$ Co + $3.0\,\mu m$ Zn$)_n$	2	4	−0.475	93.5	−1.200	6.5
$3.0\,\mu m$ Zn + $(3.0\,\mu m$ Co + $3.0\,\mu m$ Zn$)_n$	2	5	−0.350	77.7	−1.150	22.3
$(3.0\,\mu m$ Co + $0.3\,\mu m$ Zn$)_n$	4	8	−0.480	96.3	−1.300	3.7
$(0.3\,\mu m$ Co + $3.0\,\mu m$ Zn$)_n$	4	8	−0.460	52.8	−1.150	47.2

*Table 2. Characteristic features of different type of deposits, number of layers, potentials of the stripping peak maximums and the ratio (in %) between the area of the individual stripping peaks (q^{I}, q^{II}) and the total area of both peaks ($q^{I} + q^{II}$)**

Deposit	*Number of layers* (n)	*Number of sublayers* ($2n$)	*Peak (I)* E_A^{peakI} /V vs SSE	*Peak (I)* $\frac{q^I}{q^I+q^{II}}$ /%	*Peak (II)* E_A^{peakII} /V vs SSE	*Peak (II)* $\frac{q^{II}}{q^I+q^{II}}$ /%
(0.3 μm Zn + 0.3 μm Co)$_n$	2	4	−0.600	94.0	−1.330	6.0
	20	40	−0.375	92.0	−1.225	8.0
0.3 μm Co + (0.3 μm Zn + 0.3 μm Co)$_n$	2	5	−0.575	94.0	−1.320	6.0
	24	49	−0.350	91.0	−1.180	9.0
(3.0 μm Zn + 3.0 μm Co)$_n$	2	4	−0.425	94.0	−1.280	6.0
3.0 μm Co + (3.0 μm Zn + 3.0 μm Co)$_n$	2	5	−0.330	98.0	−1.250	2.0
(3.0 μm Zn + 0.3 μm Co)$_n$	4	8	−0.450	65.0	−1.200	35.0
(0.3 μm Zn + 3.0 μm Co)$_n$	4	8	−0.400	99.0	−1.325	1.0

* The Zn–Co CMM are deposited from dual baths. The oversublayer is of Co.

cobalt sublayers at more positive potentials. When the coating is composed of four thin cobalt and four thick zinc sublayers 47.2% of the coating dissolves at more negative potential because thin cobalt sublayers cannot adequately protect the thick zinc sublayers. However, a substantial part of the zinc layers dissolve, together with the cobalt sublayers at more positive (−0.460 V) potentials.

Table 2 presents the relationships between the potential of the stripping peaks and the deposit type and the number of sublayers, when the multilayers end with a cobalt oversublayer. Coatings composed of an even number of sublayers start with a zinc and end with a cobalt sublayer. Coatings composed of an odd number of sublayers begin and end with a cobalt sublayer.

During the stripping of deposits composed of four or five 0.3 μm thick sublayers only a small part (6.0%) of the zinc dissolves at more negative potentials (−1.330 and −1.320 V). The remaining amount of zinc and all the cobalt dissolve at more positive potentials (−0.600 and −0.575 V). When the coating begins and ends with a cobalt sublayer, both potentials shift in the positive direction as compared with the potentials of coatings starting with zinc and ending with a cobalt sublayer. Similar behaviour was observed during the stripping of coatings composed of 40 or 49 0.3 μm thick sublayers and four or five 3.0 μm thick sublayers. Results show that, in spite of the thickness, the cobalt oversublayer protects the remaining zinc sublayers under it. As a result only a small part of the zinc dissolves through the pores of the cobalt oversublayer. The protection is most efficient when the coating starts and ends with a 3.0 μm thick Co sublayer (five sublayers). In this case only 2.0% of the coating dissolves at −1.250 V.

During the stripping of a coating, composed of four thick (3.0 μm) zinc and four thin (0.3 μm) cobalt sublayers, 35.0% of the coating (about half of the zinc) dissolves at a more negative (−1.200 V) potential. The rest of the Zn and all the cobalt dissolve at −0.450 V. The protective efficiency of cobalt sublayers is enhanced when the coating is composed of four thin (0.3 μm) zinc and four thick (3.0 μm) cobalt sublayers. In this case only 1.0% of the coating dissolves at a more negative potential (−1.325 V), that is, less than 25% of zinc. The remaining (99.0%) part of the deposit dissolves at −0.400 V. This potential is more positive, as compared with the former case, because the amount of cobalt in the coating is larger.

3.2. *Multilayer coatings deposited from single baths containing both zinc and cobalt ions*

Composition modulated Zn–Co multilayers of alternate alloy sublayers with low (1.0%) and high (6.5%) cobalt content were obtained galvanostatically. Alloy coatings containing 1% cobalt (Zn–Co1%) and 6.5% cobalt (Zn–Co6.5%) were deposited at 0.2 and 2 A dm^{-2}, respectively. The 0.3 μm thick Zn–Co1% sublayers were deposited for 7 min, and 0.3 μm thick Zn–Co6.5% for 45 s. The 3.0 μm thick Zn–Co1% sublayers were deposited for 1 h and 3.0 μm Zn–Co6.5% for 7 min.

Figure 2 shows voltammograms for potentiodynamic stripping of a coating consisting of five sublayers, each 0.3 μm thick (curves 1 and 2) or 3.0 μm thick (curves 3 and 4). Curves 1 and 3 show the current–potential dependence when the multilayer coatings end with a Zn–Co1% oversublayer and curves 2 and 4 when the multilayer coatings end with a Zn–Co6.5% oversublayer. When the sublayers are 0.3 μm thick, three stripping peaks appear on the voltammograms and when the individual sublayers are 3.0 μm thick, only one large anodic peak is present. The stripping peaks are at potentials within the potential range of the stripping peaks of CMM coatings deposited from dual baths.

A similar character is displayed by the stripping curves of coatings consisting of 4, 40 and 49 sublayers with equal sublayer thickness, as well as coatings composed of alternating thin (0.3 μm) and thick (3.0 μm) sublayers.

Table 3 shows the relationship between the potential of the stripping peaks and the deposit type and

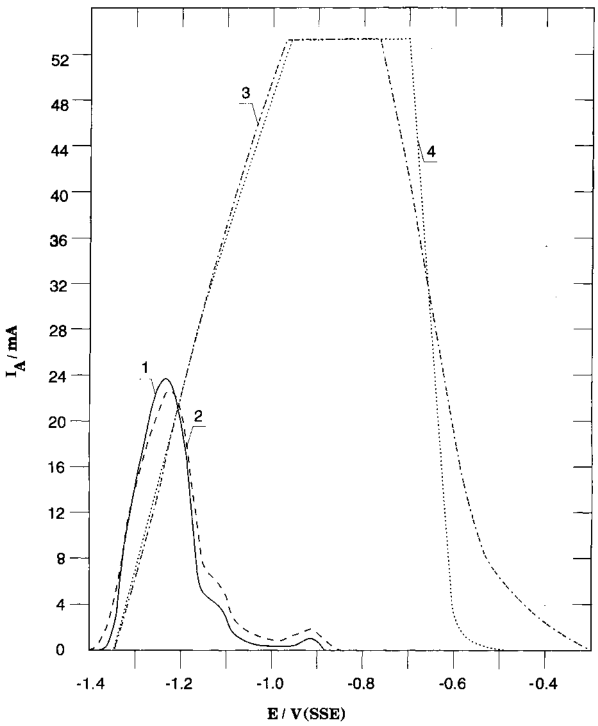

Fig. 2. Stripping voltammograms of Zn–Co alloy coatings consisting of five sublayers deposited from single bath, each of thickness 0.3 μm (1,2) or 3.0 μm (3,4): (1) coating ends with a Zn–Co1% oversublayer; (2) coating ends with a Zn–Co6.5% oversublayer; (3) coating ends with a Zn–Co1% oversublayer; (4) coating ends with a Zn–Co6.5% oversublayer.

the number of sublayers when the multilayers end with a Zn–Co1% oversublayer. Table 4 shows the same dependence when the multilayers end with a Zn–Co6.5% oversublayer. In both cases when the number of sublayers is small (4 and 5) and the thickness is 0.3 μm, the stripping peaks are three, while when the number is 40 or 49, the stripping peak is only one. With increase in the number of sublayers the dissolution potential is shifted positively as a result of the increase in the amount of deposited alloy. The same dependence is observed when the individual sublayer thickness is 3.0 μm. When thick (3.0 μm) Zn–Co6.5% and thin (0.3 μm) Zn–Co1% or thin (0.3 μm) Zn–Co6.5% and thick (3.0 μm) Zn–Co1% sublayers are alternated the dissolution potentials of the coatings are practically equal.

4. Conclusions

CMM coatings obtained from dual baths containing either Zn^{2+} and Co^{2+} mainly dissolve at potentials much more positive compared with the dissolution potentials of pure zinc coatings and are close to those of pure cobalt coatings. This effect is very pronounced when the coating ends with a cobalt oversublayer. With the increase in the number of sublayers, regardless of their thickness and sequence, the potentials of the stripping peaks are shifted positively.

Table 3. Characteristic features of different type of deposits, number of layers, potentials of the stripping peak maximums and the ratio (in %) between the area of the individual stripping peaks (q^{I}, q^{II}) and the total area of both peaks ($q^{I} + q^{II}$). The Zn–Co CMM are deposited from single bath. The oversublayer is of Zn–Co1%

Deposit	*Number of layers* (*n*)	*Number of sublayers* (2*n*)	$E_A^{Peak(i)}$ /V vs SSE
(0.3 μm Zn–Co6.5% + 0.3 μm Zn–Co1%)$_n$	2	4	−0.925, −1.130*, −1.260
	20	40	−0.950
0.3 μm Zn–Co1% + (0.3 μm Zn–Co6.5% + 0.3 μm Zn–Co1%)$_n$	2	5	−0.910, −1.120*, −1.230
	24	49	−0.900
(3.0 μm Zn–Co6.5% + 3.0 μm Zn–Co1%)$_n$	2	4	−0.700*, −1.000
3.0 μm Zn–Co1% + (3.0 μm Zn–Co6.5% + 3.0 μm Zn–Co1%)$_n$	2	5	−0.875
(3.0 μm Zn–Co6.5% + 0.3 μm Zn–Co1%)$_n$	4	8	−0.940
(0.3 μm Zn–Co6.5% + 3.0 μm Zn–Co1%)$_n$	4	8	−0.900

* inflexion point.

Table 4. Characteristic features of different type of deposits, number of layers, potentials of the stripping peak maximums and the ratio (in %) between the area of the individual stripping peaks (q^{I}, q^{II}) and the total area of both peaks ($q^{I} + q^{II}$). The Zn–Co CMM are deposited from single bath. The oversublayer is of Zn–Co6.5%

Deposit	*Number of layers* (*n*)	*Number of sublayers* (2*n*)	$E_A^{Peak(i)}$ /V vs SSE
(0.3 μm Zn–Co1% + 0.3 μm Zn–Co6.5%)$_n$	2	4	−0.920, −1.120*, −1.240
	20	40	−0.925
0.3 μm Zn–Co6.5% + (0.3 μm Zn–Co1% + 0.3 μm Zn–Co6.5%)$_n$	2	5	−0.900, −1.110*, −1.225
	24	49	−0.875
(3.0 μm Zn–Co1% + 3.0 μm Zn–Co6.5%)$_n$	2	4	−1.000
3.0 μm Zn–Co6.5% + (3.0 μm Zn–Co1% + 3.0 μm Zn–Co6.5%)$_n$	2	5	−0.825
(3.0 μm Zn–Co1% + 0.3 μm Zn–Co6.5%)$_n$	4	8	−1.060
(0.3 μm Zn–Co1% + 3.0 μm Zn–Co6.5%)$_n$	4	8	−0.860* −1.080

* inflexion point.

CMM coatings obtained from a single bath containing both Zn^{2+} and Co^{2+} dissolve at more positive potentials, as compared with pure zinc coatings but much more negative than the dissolution potentials of pure cobalt coatings. With the increase in the sublayer number, regardless of the thickness and sequence, the dissolution potentials are shifted in the positive direction.

Acknowledgement

The authors wish to acknowledge financial assistance by the National foundation "Scientific investigation", Bulgaria.

References

[1] D. Tench and J. White, *Metall. Trans. A* **15A** (1984) 2039.

[2] C. Ogden, *Plat. Surf. Finish.* **5** (1986) 130.

[3] J. Yahalom and O. Zadok, *J. Mater. Sci.* **22** (1987) 499.

[4] *Idem*, *US Patent 4 652 348* (1987).

[5] L. Bennett, D. Lashmore, M. Dariel, M. Kaufman, M. Rubinstein, P. Lubitz, O. Zadok and J. Yahalom, *J. Magn. Magn. Mater.* **67** (1987) 239.

[6] U. Atzmony, L. Swartzendruber, L. Bennett, M. Dariel, D. Lashmore, M. Rubinstein and P. Lubitz, *ibid.* **69** (1987) 237.

[7] A. Despic and V. Jovic, *J. Electrochem. Soc.* **134** (1987) 3004.

[8] D. Lashmore and M. Dariel, *ibid.* **135** (1988) 1218.

[9] A. Despic, V. Jovic and S. Spaic, *ibid.* **136** (1989) 1651.

[10] S. Menezes and D. Anderson, *ibid.* **137** (1990) 440.

[11] D. Tench and J. White, *ibid.* **137** (1990) 3061.

[12] J. Celis, A. Haseeb and J. Roos, *Trans. Inst. Metal. Finish.* **70** (1992) 123.

[13] D. Simunovich and M. Schlesinger, *J. Electrochem. Soc.* **141** (1994) L10.

[14] A. Haseeb, J. Celis and J. Roos, *ibid.* **141** (1994) 230.

[15] C.-C. Yang and H. Cheh, *ibid.* **142** (1995) 3034.

[16] *Idem*, *ibid.* **142** (1995) 3040.

[17] R. Intrater and J. Yahalom, *J. Mater. Sci. Lett.* **12** (1993) 1549.

[18] D. Tench and J. White, *J. Electrochem. Soc.* **138** (1991) 3757.

[19] R. Weil, C. Nee and W. Chang, *Metallurg. Trans. A* **19A** (1988) 1569.

[20] G. Barral and S. Maximovich, *Colloque de physique, Colloque C4* **51** (1990) 291.

[21] M. Kalantary, G. Wilcox and D. Gabe, *Electrochim. Acta* **40** (1995) 1609.

[22] L. Goldman, B. Blanpain and F. Spaepen, *J. Appl. Phys.* **60** (1986) 1374.

[23] C. Ross, L. Goldman and F. Spaepen, *J. Electrochem. Soc.* **140** (1993) 91.

[24] G. Wouters, M. Bratoeva, J.-P. Celis and J. Roos, *J. Electrochem. Soc.* **141** (1994) 397.

[25] G. Wouters, M. Bratoeva, J.-P. Celis and J. Roos, *J. Electrochim. Acta* **40** (1995) 1434.

[26] *Bulgarian Patent 39 402* (1978).