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Growth modes of electrodeposited cobalt

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Abstract

Structure, morphology and electrokinetics in cobalt electrocrystallisation from sulphamate electrolytes, either without or with addition of boric acid, are studied and an interpretation of the structure characteristics and growth modes of electrodeposited cobalt is proposed. The correlation between crystallographic structure and electrokinetic behaviour, analysed by short galvanostatic pulses over-imposed during steady-state growth at fixed current density, is investigated, pointing out the main factors which affect structure and texture of electrodeposits and emphasising the electrolyte pH influence. Three well-defined growth modes are recognised and univocally related to the transient electrokinetic parameters. Growth structures characterised by low crystallinity and/or texture modifications occur in relation with the disturbance of the hydrogen discharge reaction or as a result of ageing of not-buffered electrolyte.

The basic growth modes are classified as follows: outgrowth or perpendicular growth, in condition of surface stabilisation of hydrolysed species resulting in low nucleation activity and growth of relatively large-grained columnar deposits; lateral growth, when hydrolysed species are stable in the bulk solution and cellular crystallisation occurs as a consequence of full surface coverage by discharge intermediates and precipitation of insoluble hydrolysis products at grain boundaries; cluster growth, in the presence of boric acid, in conditions of nucleation control, possibly related to the formation of adsorbed complexes stabilised at the surface by boric acid. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Cobalt electrodeposition; Electrodeposits structure; Electrodeposits texture; Electrokinetics; Iron group metals

1. Introduction

The easy occurrence of preferred orientation (PO) in electrodeposited (ECD) iron group metals has stimulated a number of investigations, without, however, achieving the stage of a comprehensive view. A general and exhaustive interpretation, centred on Fischer's concept of inhibition [1], was proposed for nickel electrocrystallisation from Watts's electrolyte [2,3] and later extended to cover the different texture types from simple sulphate and chloride solutions [4,5].

Cobalt electrocrystallisation has been far less studied compared to Ni, although ECD Co and Co alloys are eligible materials for applications ranging from magnetic media and devices [6] to wear and corrosion resistant coatings. Advances in the comprehension of the factors and

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E-mail address: antonello.vicenzo@polimi.it (A. Vicenzo). ¹ ISE member. mechanism participating in Co electrocrystallisation is expected to contribute to the systematic understanding of the structure–properties correlation of ECD Co and Co alloys, as stressed in a recent review [7].

Electrolytic Co crystallises with both hexagonal closed packed (hcp, α -Co), the stable allotropic modification at temperature below 417 °C, and face centred cubic (fcc, β -Co) lattice structure, as first reported by Hull [8]. The solution pH was shown to be the most important parameter in determining the structure of ECD Co by Kersten [9]. Pangarov and Rashkov [10] determined the relations between the main operative conditions and electrodeposits structure: β -Co formation is favoured by low temperature, high current density (cd) and low pH. Polukarov [11] came to similar conclusions. These early results were confirmed by several authors [12–14].

The formation of β -Co by electrodeposition was studied in details and still remains a research topic of primary relevance, although in recent years the attention has been particularly focused on phase selection as related to substrate in-

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fluence [15,16] and deposition conditions [15,17,18] rather than on the mechanism of phase formation, for which the reference papers are still those of Gaigher and Van der Berg [19] and of Nakahara and Mahajan [20].

The first extensive reports on the crystal structure of ECD α -Co appeared in 1966, by Cadorna and Cavallotti [12] and by Pangarov and Vitkova [21]. According to the latter, the experimental results were in substantial agreement with the theory of two-dimensional nucleation [22]. The following investigations were almost exclusively focused on deposition from Watts's type electrolyte or from buffered sulphate solution. Deposits having two-phase composition show a hcp [11.0] + fcc [110] texture, from buffered sulphate [13,21,23,24] or sulphamate [12] solution, in agreement with the early observation of Finch et al. [25]. With increase of pH the structure becomes completely of the α -phase and deposits texture depends mainly on solution pH [12,23–26] and, to a minor extent, on temperature [23] and cd [27]. The prevailing orientations and their stability with respect to the operative conditions are characterised in details for both sulphate [12,13,23,24,28] and chloride based electrolytes [29].

Early attempts to interpreter the growth modes of ECD Co followed Reddy's views on Ni electrocrystallisation [30]. The different growth textures were explained as consequence of competitive adsorption between hydrogen and intermediate species [23] or classified according to growth conditions related to different degree of inhibition [13]. Subsequently, the main importance of the electrolyte pH was recognised. It was suggested [20] or explicitly stated [19] that the surface pH and the related chemical phenomena at the cathode surface were the major factors responsible for the development of different textures [26,31]. The structural bearing of hydrolytic phenomena received further support from the work of Croll [26], who reported that, depositing from CoSO₄ electrolyte, in the absence of H₃BO₃ a sharp change from [10.0] + [11.0] to [00.1] PO takes place at pH about 4 within a short range, while when H₃BO₃ is present, the [10.0] + [11.0] PO weakens gradually as the pH raises and the transition pH is higher, about 6.4. The possibility of obtaining the three main growth textures of α -Co by autocatalytic deposition [32] and the assessment of the conditions giving Co cellular growth [33,34] with strong [00.1] texture definitely pointed out the decisive contribution of reactive hydrolysis in determining the deposits structure.

From the standpoint of the phenomenological comprehension, the literature about Co electrodeposition provides the elements for understanding the relationship between operative conditions and crystallographic structure of electrolytic Co. On the ground of this well-established knowledge, the main objective of the present work is to investigate the correlation between structure and kinetics in Co electrocrystallisation from sulphamate solutions. We have already shown that the electrokinetic behaviour is influenced by hydrolysis conditions at the surface [35] and that the structure–kinetics relationship in Co electrodeposition from sulphamate bath can be rationalised on the basis of pH and boric acid influence [36]. In the present paper the structure–kinetics correlation is analysed in details and explained considering the role of the different electrolyte species involved in the growth process at the cathode.

2. Experimental

The plating solutions were prepared from analytical grade chemicals and distilled water. Electrolytes with 1 M Co²⁺ concentration were prepared from Co carbonate and sulphamic acid (in the following, the symbol σ stands for the sulphamate anion, $H_2NO_3S^-$). H_3BO_3 , in concentration 0.4 or 0.5 M, CoCl₂ and sulphamid were added in some instances as outlined in Table 1, where composition and operation conditions for all plating baths are listed. The electrolytes were pre-treated to eliminate organic impurities with active charcoal (1 h, 80 °C); in addition, some solutions were pre-treated with electrolysis at low current $(cd < 1 \text{ mA cm}^{-2})$ and with large cathodic area. Since no detectable differences were noticed between same baths before and after this treatment, it was thereafter omitted. Plating baths pH was adjusted by addition of either cobalt hydroxy-carbonate or sulphamic acid. The substrates were either brass sheets coated with about 3 µm ACD NiP or brass sheets mechanically polished with 1200 grit emery-paper. Either a dilute HCl (NiP coated brass) or H σ (brass) etch, followed by washing with distilled water and drying with nitrogen gas, was used immediately before plating. High purity Co was used as anode.

Phase structure and texture of deposits were determined by X-ray diffractometry (XRD) with Cu K α radiation and a powder goniometer. All electrodeposits were thick enough to show the crystallographic orientation imposed by the bath (not less than 20 μ m). In order to characterise texture modification of α -Co deposits with electrolyte composition (namely, pH in the range 2.7–6 and boric acid addition), the volume fraction M_{hkl} of different texture components was estimated by the equation [37,38]:

$$M_{hkl} = \frac{F_{hkl}}{\sum_{hkl} F_{hkl}}$$

Table 1							
Composition	and	operative	conditions	of the	electrolytes	$(NH_2SO_3: o$	J)

Solution	pН	<i>T</i> (°C)	cd $(mA cm^{-2})$
Coσ ₂ 1 M	1.8-6	30	4-40
$Co\sigma_2$ 1 M–H ₄ N ₂ O ₂ S (sulphamid) 5 mM	6	30	5-20
$Co\sigma_2$ 1 M–H ₃ BO ₃ 0.4 M	2.5-4.8	30	10
$Co\sigma_2 1 M - H_3 BO_3$	4.3	30	10-20
0.5 M-CoCl ₂ 0.1 M			
Coo ₂ 1 M–H ₃ BO ₃	5.2	30	10
0.5 M-CoCl ₂ 0.1 M			

where the texture index F_{hkl} for(h k l) plane is given by the expression:

$$F_{hkl} = \frac{I_{hkl}/I_{hkl}^{\mathrm{R}}}{(1/n)\sum_{hkl}I_{hkl}/I_{hkl}^{\mathrm{R}}}$$

 I_{hkl} is the measured intensity of reflection (h k l); I_{hkl}^{R} is the reflection intensity of a random powder sample; and *n* is the number of measured reflections. This procedure is valid on the assumption that only crystals with orientation along the measured directions occur, that is, (10.0), (00.2), (10.1), (11.0); and that a low or nil volume fraction of β -Co is present so as not to contribute appreciably to the reflection intensities of the (00.2) and (11.0) lines.

Surface morphology of thick deposits was investigated by scanning electron microscopy (SEM). Atomic force microscopy (AFM) in conjunction with glancing angle XRD analysis was used to characterise the initial stages of growth of Co thin films electrodeposited from pH 4 buffered and not-buffered solution at 10 mA cm⁻² and 30 °C. Thin films of up 1 μ m thickness were deposited on Si(100)/TiN/Cu substrate; the Cu seed layer was 100 nm thick and [111] textured.

Potentiodynamic, steady-state and transient galvanostatic experiments were carried out in a standard three-electrode configuration, with either an Ag/AgCl reference electrode (RE) in connection to the working electrode with a lateral-channel Piontelli probe [39] (potentiodynamic and steady-state galvanostatic measurements) or a Pt RE (transient measurements). A Model 273A EG&G PAR and an AMEL System 5000 potentiostat/galvanostat were used. Potentiodynamic runs (scan rate 0.1 mV s⁻¹) and constant current potentiometry were performed on electrodes previously coated (about $3 \mu m$) in the same electrodeposition bath. No ohmic correction was made, when using the Piontelli probe.

The kinetic behaviour during deposition was investigated with the secondary current pulse (SCP) technique [40,41]. The principle of the SCP method is that of a direct current relaxation technique in which the electrode, which is kept in a steady-state at fixed deposition cd, is perturbed by a current pulse and the relaxation transient is recorded and analysed by non-linear fitting procedure in order to estimate the parameters of the equivalent circuit of the electrode system, as described later in this article.

SCP measurements were performed over-imposing short (4–6 ms) square current pulses ranging from $(i_D + 10)$ to $(i_D + 50) \text{ mA cm}^{-2}$ during deposition at i_D cd. Before measurements, cobalt was deposited from the bath under study at i_D for 30 min. Pulses were applied every 3–5 min time interval depending on the bath; interface and growth stability was checked by monitoring the cathode potential during deposition. SCP samples were always subjected to XRD analysis and SEM observation showing no differences with respect to samples prepared in standard conditions. Ohmic drop in solution, η_{ω} , could be readily determined from the

transients; a linear relationship between η_{ω} and $(i_{\rm P} - i_{\rm D})$ was found in all instances.

3. Results

3.1. Structure and morphology of ECD Co from not-buffered solutions

Structure and texture of Co deposited from $\text{Co}_2 \ 1 \text{ M}$ solution, at 30 °C and cd in the range up to 40 mA cm⁻², is mainly influenced by the solution pH.

In the acidic region at pH < 2.5, deposits crystal structure is characterised by the presence of both α and β -Co, with high density of stacking faults and lattice strain, as shown by (10.0) peak asymmetry [42] and by peaks broadening [43]. In Fig. 1A, the surface morphology of a 20 µm thick coating (pH 1.8, cd $40 \,\mathrm{mA}\,\mathrm{cm}^{-2}$) shows coexistence of different features related to the two-phase structure: elongated ridge-shaped crystals embedded in a fine-grained matrix. The transition from β to α -Co occurs in the pH range 2.5-3.0. Coatings obtained in this pH range show a faulted hcp crystallographic structure, characterised by (10.1) line broadening [44], low crystallinity and a faint two-fold [11.0] and [10.0] PO; no formation of β -Co in appreciable amount occurs in this pH range, according to XRD analysis, that is the (200) cubic diffraction line is either very weak, for the low pH values in the above range, or not observed; however, even in the later case, the presence of a low volume fraction of β -Co, as a finely disperse phase, cannot be ruled out.

Increasing the electrolyte pH, a transition occurs from the two-fold [11.0] and [10.0] PO to a strong [11.0] PO at pH $3.2(\pm 0.2)$. Deposits with [11.0] PO are obtained at pH in the range 3.2-5.7 and cd 5-40 mA cm⁻². The surface morphology of α -Co deposits with strong [11.0] PO is shown in Fig. 1B and C and Fig. 2A and B. The characteristic features change with pH, from dihedral grains, resulting from piling up of outgrowing basal planes, in the more acidic range; to pyramidal grains of four or five-fold symmetry at higher pH, of size 0.5-2 µm, increasing as pH decreases. This characteristic crystal habit is shown in Fig. 2A and B by surface SEM micrographs on 20 µm thick coatings electrodeposited from a pH 4 Co σ_2 1 M electrolyte at 10 mA cm⁻² and 30 °C, either without or with the addition of Cl⁻ 0.2 M, respectively. Growth of pentagonal pyramids is a consequence of multi-twinned crystallite formation, as already observed for Ag [45,46] and Ni [47,48] fcc metals. Similar morphological features were reported by Weil and co-workers [13] and Winand and Scoyer [29] for [11.0] textured deposits.

The observed correlation between electrolyte pH and [11.0] PO is influenced by electrolyte ageing in the laboratory environment at room temperature. Ageing results in the suppression of the [11.0] PO and the formation of a faint two-fold [10.0] and [11.0] texture, which corresponds to the growth structure observed depositing from electrolytes at pH below about 3.2; eventually, coatings structure changes



Fig. 1. Surface SEM micrographs of Co deposits from $Co\sigma_2$ 1 M, at 30 °C for 2 h. (A) pH 1.8, 40 mA cm⁻² (20k×); (B) pH 3.2 (20k×); and (C) pH 4.5 (50k×), both at cd 10 mA cm⁻².



Fig. 2. Surface SEM micrographs of Co deposits from $Co\sigma_2 \ 1 \text{ M}$, at cd 10 mA cm^{-2} , $30 \degree \text{C}$, for 2 h. (A) pH 4.5 (50k×); (B) +CoCl₂ 0.1 M, pH 4 (30k×); and (C) +H₄N₂O₂S 5 mM, pH 6 (50k×).

into a weak [00.1] PO and may further evolve towards a quasi-amorphous state. According to our observations, these changes occur over a variable time span up to several months. An example of such structure evolution is presented in Fig. 3, where XRD patterns of Co deposits from a simple Co σ_2 1 M solution at 10 mA cm⁻² and 30 °C are shown. A freshly prepared electrolyte of pH 5 gives deposits with [11.0] PO (pattern A in Fig. 3); at pH 3.3 (pattern B) deposits with the two-fold [11.0] and [10.0] PO; the same solution, after 6 weeks ageing at room temperature and pH 3.3, gives coatings showing a highly defective [00.1] P.O. (pattern C). This time-variant behaviour is apparently related to the evolution of hydrolysis reactions in the plating solution, resulting in the formation of hydroxyl complexes, polynuclear or even polymeric species [49]. The attribution of solution ageing to hydrolytic phenomena is supported by the observation that 0.1 M CoCl₂ addition to pH 4 electrolyte greatly stabilises the [11.0] textured growth mode, which is practically not affected by ageing time: [11.0] textured coatings were obtained from a bath of such composition over a period of 24 months. The vanishing of ageing effects in the presence of chloride can be readily understood as a result of chloro-cobalt and/or chloro-hydroxy-cobalt complexes, which are expected to appear as stable species at such Cl⁻ concentration, similarly to the case of nickel [50], thus influencing the hydrolytic speciation in the Co sulphamate electrolyte.



Fig. 3. XRD pattern of Co deposits from $Co\sigma_2 1 M$ (10 mA cm⁻², 2 h, 30 °C). (A) freshly prepared solution, pH 5; (B) idem, pH 3.3; and (C) after 6 weeks ageing, at pH 3.3.

This time dependent behaviour related to slow hydrolysis reactions affects also deposits nucleation: after six months ageing time, a pH 4 solution gives strong [00.1] PO on 100 nm thick [1 1 1] textured Cu film, sputtered on Si wafer; on the other hand, a heavily defective [00.1] structure is obtained on brass coated with ACD NiP.

The [00.1] PO is usually obtained from pure sulphate or sulphamate solutions at high temperature and pH, with some misorientation shown by the appearance of the (10.1) reflection. A [00.1] texture at low temperature and pH 5 was previously reported by Pangarov as an exception to the theory of two-dimensional nucleation [21]. According to previous findings [33], the [00.1] texture can be obtained from pure $Co\sigma_2$ 1 M solution at pH 6 with high perfection, in conditions of cellular growth, that is directional crystallisation of needle shaped crystallites with basal plane parallel to the surface, isolated one from the other by precipitated hydroxides or basic salts. The addition of sulphamid 5 mM strongly stabilises this growth texture, giving bright and smooth deposits with very high [00.1] PO, even at room temperature. Surface morphology of these deposits is shown in Fig. 2: grains are very small and roundish, with 50-100 nm diameter; similar values for the crystallite size, in the range from 80 to 100 nm, are derived from (00.2n) lines broadening according to the Williamson-Hall method [51], as expected for the condition of cellular growth.

XRD patterns representative of the structure of cobalt coatings electrodeposited from not-buffered $Co\sigma_2$ electrolytes at changing pH are shown in Fig. 4. The texture change occurring in α -Co deposits from not-buffered solutions as the electrolyte pH is varied in the range 2.7–5.7 is summarised in Fig. 5A by the change of the [*h k l*] orientation volume fraction.

3.2. Structure and morphology of ECD Co from buffered solutions

Co deposits from simple solutions buffered with boric acid, $Co\sigma_2 \ 1 \text{ M}$, $H_3BO_3 \ 0.4 \text{ or } 0.5 \text{ M}$, at pH 3.8–4.8, 30 °C and 10 mA cm⁻², have a characteristic two-component [11.0] + [10.0] texture, in the following referred to as "mixed texture" [27]. XRD patterns show strong reflections for (10.0) and (11.0) planes and a weak (20.1) peak; (00.2) and (10.n) lines are absent, contrary to the case of Co coat-



Fig. 4. XRD patterns of Co coatings electrodeposited on brass/NiP substrate at 10 mA cm⁻² (pH from 2.5 to 6) and 40 mA cm⁻² (pH 1.8) and 30 °C from Co σ_2 1 M electrolytes at varying pH. The deposition time was 2 h at 10 mA cm⁻² and 45 min at 40 mA cm⁻².



Fig. 5. Change of the [hkl] orientation volume fraction for ECD α -Co vs. the electrolyte pH. Co deposition from $\text{Cos}_2 \ 1 \text{ M}$ (A) and from $\text{Cos}_2 \ 1 \text{ M}$, H₃BO₃ 0.4 M solution and (B) at 10 mA cm⁻² and 30 °C.

ings from not-buffered electrolytes with the above-called two-fold [10.0] + [11.0] PO. The surface morphology is characterised by randomly arranged 2–5 μ m long ridges, possibly curved, consisting of fine sub-grains (see Fig. 6A



Fig. 7. XRD patterns of Co coatings electrodeposited on brass/NiP substrate at 10 mA cm^{-2} and $30 \text{ }^{\circ}\text{C}$ from $\text{Co}\sigma_2 1 \text{ M}$, $\text{H}_3\text{BO}_3 0.4 \text{ M}$. (A) pH 3.6; (B) pH 3.2; (C) pH 2.7; and (D) pH 1.8.

and B). The characteristic morphology of the mixed texture was described by Froment and co-workers [27,52]: the two symmetrical halves of the ridged grains were shown by electron diffraction to be differently oriented, one with [10.0] axis, the other with [11.0] axis normal to the base.

Fig. 7 presents XRD patterns of Co deposits from $Co\sigma_2$ 1 M, H₃BO₃ 0.4 M and pH 1.8-3.6. A few significant modifications of the mixed structure should be pointed out: the (10.1) peak appears at pH < 3.5; the (00.2) reflection intensity increases with decreasing pH below 3.2, with evidence of β -Co formation at pH < 2.8, as shown by the appearance of the (200) cubic line in XRD patterns. Correspondingly, as shown in Fig. 5B, the volume fraction of the [10.0] orientation decreases, whilst that of the [11.0] orientation increases, also as a possible spurious contribution from the [110] β -Co component. These structural changes are suggestive of the progressive formation of β -Co as pH decreases, through an intermediate region where accumulation of growth defects initiate the α to β -Co structure transition. In particular, the appearance of the (00.2) + (111)reflection at pH below 3.2 points to the destabilising effect of the hydrogen evolution reaction on the mixed structure, which can accommodate most compact planes only normal to the surface.



Fig. 6. Surface SEM micrographs of Co deposits from $Co\sigma_2 1 M$, $H_3BO_3 0.4 M$, after 2 h deposition at 10 mA cm^{-2} , and $30 \degree C$. (A) pH 4 (20k×); (B) pH 4.8 (20k×); and (C) +CoCl₂ 0.1 M, pH 5.2 (20k×).



Fig. 8. Glancing angle XRD patterns of Co deposits from $Co\sigma_2 \ 1 M$ (lower curve) and $Co\sigma_2 \ 1 M$, H₃BO₃ 0.4 M (upper curve) on Si/TiN/Cu substrate, at pH 4, 10 mA cm⁻², and 30 °C, after 60 and 120 s deposition time, respectively (S: substrate).

Deposits obtained from solutions containing also $CoCl_2$ 0.1 M, at pH 4.3 or 5.2 show the same mixed structure with the [11.0] orientation component prevailing as cd increases. Surface morphology, as shown in Fig. 6C, is slightly changed, consisting of smaller ridges, the size of 2 μ m or less, either straight or bent, often gathered in thick bundles.

3.3. Early stages of growth

Fig. 8 shows glancing angle XRD patterns of Co thin deposits from $Co\sigma_2 1$ M solutions, in the absence or presence of $H_3BO_3 0.4$ M, on Si/TiN/Cu [1 1 1], at pH 4, 10 mA cm⁻², and 30 °C, after 60 and 120 s deposition, respectively. From the 6-month-aged not-buffered solutions, a [00.1] texture is already emerging, also as a result of epitaxial growth on the Cu [1 1 1] substrate; from the buffered solution, the mixed texture is obtained, despite the adverse substrate influence. After 300 s deposition, as shown in Fig. 9 by XRD patterns of Co deposits on the same substrate and in the same operative conditions, a strong [00.1] PO is observed from the aged not-buffered solution, while from the buffered solution the mixed texture [10.0] + [11.0] prevails.



Fig. 9. XRD patterns of Co deposits from $Co\sigma_2 \ 1 M$ (upper curve) and $Co\sigma_2 \ 1 M$, $H_3BO_3 \ 0.4 M$ (lower curve) on Si/TiN/Cu substrate, at pH 4, 10 mA cm⁻², and 30 °C, after 300 s deposition time (S: substrate).



Fig. 10. Three-dimensional AFM images of the surface topography of Co thin layer on Si/TiN/Cu substrate, after deposition for 60 (left) and 300 s (right) from a pH 4, $Co\sigma_2$ 1 M solution at 30 °C and 10 mA cm⁻².

AFM surface topography gives further support to XRD investigations. Fig. 10 shows AFM images of Co thin films obtained from the aged not-buffered electrolyte, after 60 and 300 s deposition time. These films, obtained with 94% current efficiency, are discontinuous even at 200 nm thickness and characterised by irregularly sized and shaped grains, resulting from the coalescence of smaller crystallites. After 300 s deposition, grain size increases and grain boundaries appear well defined around single grains in relief, while the outer projection of single grains remains unchanged, compared to the 200 nm thick layer.

In Fig. 11, AFM images of thin Co films from $Co\sigma_2 \ 1 \text{ M}$, $H_3BO_3 \ 0.4 \text{ M}$, pH 4 solution, are shown. After 10 s deposition time, at 10 mA cm⁻² and 30 nm nominal thickness, the surface shows small crystallites the size of 100 nm or less, forming a continuous layer. The morphology characteristic of the mixed texture, with prismatic grains in the shape of ridges, is already observed in this early stage of growth. After 20 s deposition, at the same cd and with 60 nm nominal thickness, AFM topography shows a continuous surface of similar morphological features; grain size is only slightly increased. After 300 s deposition, at 1 μ m nominal thickness, the characteristic surface morphology of [10.0] + [11.0] mixed texture deposits is definitively shaped.

3.4. Electrokinetic behaviour

The SCP transient technique was used to characterise interface phenomena during Co deposition from buffered and not-buffered solution at changing pH.

The overvoltage transient during SCP measurements is described with a two terms equation: the first resulting from the equivalent circuit of the potentiometric cell (consisting of the parallel of a non-linear resistor with Tafel characteristic and a variable adsorption pseudo-capacitance); the second from a linearised Sand-type contribution. The following equation of the overpotential transient results [40,41]:

$$\eta = B_{\rm T} \ln \left[\frac{i_{\rm P}}{i_{\rm D}} - \frac{i_{\rm P} - i_{\rm D}}{i_{\rm D}} \exp \left(- \frac{i_{\rm D} t}{B_{\rm T} C_{\rm ads}} \right) \right] + \frac{RT}{zF} \sqrt{\frac{t}{\tau}}$$
(1)

with parameters: $B_{\rm T}$ (mV dec⁻¹) the transient Tafel slope, $C_{\rm ads}$ (μ F cm⁻²) the adsorption pseudo-capacitance, τ (ms) the relaxation time; $i_{\rm D}$ the deposition cd and $i_{\rm P}$ the pulse cd. $B_{\rm T}$ is related to the asymptotic value reached after charging;



Fig. 11. Three-dimensional AFM images of the surface topography of Co thin layer on Si/TiN/Cu from a pH 4, $Co\sigma_2$ 1 M, H_3BO_3 0.4 M, solution (30 °C and 10 mA cm⁻²). From left to right: 10, 20 and 300 s deposition time.

if a steady overvoltage value is not reached at the end of the pulse, when phenomena preceding or parallel to the charge transfer step influence the cathodic process, $B_{\rm T}$ can be inferred from the time behaviour of the transient, introducing the second term for the overpotential. The capacitance behaviour at the electrodic surface is related to the nature and amount of adsorbed electroactive species and the expression $C_{ads} \exp(\eta/B_T)(d\eta/dt)$ is assumed for the capacitive cd, accounting for the influence of the surface overpotential η on the pseudo-capacitance change at the electrode. With regard to the $t^{1/2}$ term, neither diffusive nor convective effects are likely to affect the transient behaviour at the electrode in a time length as short as 6 ms, with high concentration of reactants and slow electrode reactions; then, the SCP method, in our experimental conditions, can effectively separate the surface phenomena from mass-transport effects. Consequently, except for a few cases, namely when the hydrogen discharge reaction plays an important role as a side-reaction, the $t^{1/2}$ term is representative of adsorption effects involving the modification of the surface concentration of either reactant or inhibiting species [53]. In fact, a linear relationship between $\tau^{1/2}$ and the reciprocal of $(i_{\rm P} - i_{\rm D})$ was observed, while the product of $\tau^{1/2}$ times $i_{\rm P}$ or $(i_{\rm P} - i_{\rm D})$ was not constant, showing that the observed phenomena do not conform to the case of electrode process controlled by diffusion [54]. Fitting of the experimental data was carried out by a non-linear least-square optimisation procedure; a good agreement was always found between experimental and theoretical transient, with Chi-square values as a rule in the range 0.2–0.01.

Fig. 12 shows the influence of pH upon SCP parameters for $Co\sigma_2$ 1 M solution and $Co\sigma_2$ 1 M, H₃BO₃ 0.4 M solutions. The reported values are the average of 5–10 measurements at changing pulse cd in the range from 20 to 60 mA cm^{-2} ; the error bar refers to the difference between the average and the highest and lowest value obtained.

For simple sulphamate solutions, the SCP parameters $B_{\rm T}$ and $C_{\rm ads}$ are similarly influenced by pH change. In the acidic region $B_{\rm T}$ is in the range 2RT/F, then decreases abruptly in the pH range 3–3.4 and levels to 70 mV dec⁻¹ at higher pH; $C_{\rm ads}$ starts from about 100 μ F cm⁻² at low pH, depending on the rate of hydrogen evolution, becoming minimum at pH around 3.2 and raising slowly at higher pH. The transient shape is affected in a peculiar fashion: at pH < 3, the transient overvoltage does not reach a steady value at low pulse cd ($i_{\rm P}$ from 2 to 4 times $i_{\rm D}$) and the $t^{1/2}$ term is introduced to account for the observed polarisation effect; τ values range from 50 to 100 ms. This behaviour can be re-



Fig. 12. SCP parameters $B_{\rm T}$ and $C_{\rm ads}$ vs. pH for Co σ_2 1 M solution (on the left side of the graph) and for Co σ_2 1 M, H₃BO₃ 0.4 M solution (on the right). Reported values are average of 5–10 measurements at different pulse cd $i_{\rm P}$ 20, 30, 40, 60 mA cm⁻², and deposition cd $i_{\rm D}$ 10 mA cm⁻² (40 mA cm⁻² at pH 1.8), at 30 °C.

lated to adsorbed hydrogen disturbance, which fades away as the pulse cd and pH are raised. At pH > 3.2, the transient shape changes completely: the charging time becomes very short, resulting in low C_{ads} values down to 30 μ F cm⁻², and the transient overvoltage goes through a slight maximum. With increasing pH, the initial maximum disappears and a well-defined steady overvoltage is reached in less than 2 ms. Chloride addition causes a small increase of C_{ads} and B_{T} .

Aged (6 months from preparation) not-buffered sulphamate solutions at pH 3.2-3.6 shows a transient kinetic behaviour thoroughly different from that of not-aged baths of same pH. The transient shape reproduces that observed in not-aged bath at pH < 3. SCP parameters remain almost unchanged with pH: $B_{\rm T}$ in the range of 100 mV dec⁻¹ and $C_{\rm ads}$ about 45 μ F cm⁻². These values can be compared with those of not-aged electrolyte at pH < 3: B_T 110(±5) mV dec⁻¹ and C_{ads} 60(±10) μ F cm⁻². The change of the transient electrokinetic behaviour is even more remarkable for aged electrolyte at pH 6: the adsorption pseudo-capacitance increases to very high values, ranging from 150 to a maximum of about $500 \,\mu\text{F}\,\text{cm}^{-2}$ and the Tafel transient parameter $B_{\rm T}$ becomes lower than 60 mV dec⁻¹, at variance with the general behaviour summarised in Fig. 12 for not-aged simple electrolytes. In particular, the lowest $B_{\rm T}$ and the highest $C_{\rm ads}$ value are observed for electrolyte containing sulphamid 5 mM and giving strong [00.1] PO.

In the presence of H₃BO₃ 0.4 or 0.5 M, the transient electrokinetic behaviour is quite different. The SCP parameters display an opposite variation with increasing solution pH from 2.7 to 4.8: $B_{\rm T}$ increases almost linearly from about 100 to over 160 mV dec⁻¹; in the same pH range, $C_{\rm ads}$ decreases from 90 to 60 μ F cm⁻² and this change takes place over a 0.5 pH interval. In the low pH region of the above range, SCP parameters show values similar to those observed in the absence of H₃BO₃: at pH 2.7, $B_{\rm T}$ and $C_{\rm ads}$ are: 100 mV dec⁻¹ and 85(±10) μ F cm⁻², respectively; those derived for not-buffered solution at pH 2.5 and 3 are: 110 mV dec⁻¹ and 65(±10) μ F cm⁻², respectively.

On the other hand, the transient overvoltage at pH > 3.5 is greatly enhanced compared to solutions of same pH without H₃BO₃. At pH 4 or higher, SCP parameters are: $B_{\rm T}$ 160–170 mV dec⁻¹ and $C_{\rm ads}$ from 50 to 70 μ F cm⁻², the lowest value being observed at the highest pH value; τ is in the range 5–60 ms at pH 3.8, and 10–20 ms at pH 4.8. Tafel slopes, resulting from steady-state measurements in the cd range 10–100 mA cm⁻², are 110 mV dec⁻¹ (pH 4.8) and 125 mV dec⁻¹ (pH 3.8).

Chloride addition to buffered electrolytes induces a sensible increase of both C_{ads} and B_T . For Co σ_2 1 M, CoCl₂ 0.1 M, H₃BO₃ 0.5 M, at pH 5.2, SCP parameters become: B_T 180(±10) mV dec⁻¹ and C_{ads} 90(±10) μ F cm⁻². No steady overvoltage is reached within the short time of the transient and the $t^{1/2}$ term must be considered, resulting in τ values almost constant at about 6 ms. Tafel slopes from both potentiodynamic and steady-state potentiostatic measurements are 80–90 mV dec⁻¹.

4. Discussion and conclusion

The analysis of the correlation between growth modes and transient electrokinetic behaviour during deposition can give interesting insight on Co electrocrystallisation from sulphamate solution, permitting the identification of the main factors determining crystal structure and texture of Co deposits. The kinetics–structure correlation is basically determined by the adsorption behaviour of hydrolysis products, whose role as reaction intermediates was first recognised by Simonova and Rotinyan [55] and Heusler [56,57] and, later, by Lenoir and Wiart [58].

At low pH, Co structure is biphasic fcc+hcp, with possible predominance of β -Co depending on the rate of the hydrogen discharge reaction. The resulting structure is heavily faulted as a consequence of accumulation of stacking defects, possibly twin faults, on fcc {111} planes. In this growth condition, adsorbed hydrogen is the stable species at the surface and its presence gives high adsorption pseudo-capacitance and B_T in the range of 2RT/F, which is the typical value for hydrogen evolution.

The metastable fcc phase slowly vanishes increasing pH and [11.0] PO comes out, through a transition region characterised by the formation of a faulted hcp structure, with faint [10.0] and [11.0] texture. This structure is still affected by the influence of adsorbed hydrogen, as shown by the persistence of $B_{\rm T}$ in the range of 2RT/F for both not-buffered electrolytes (in the pH range 1.8-3) and buffered electrolytes (at pH 2.7-3.2). Significantly, a similar behaviour is also displayed by aged electrolytes (at pH 3.2-3.6), i.e. not-buffered solution giving coatings with degraded growth structure. The electrokinetic behaviour is the possible result of the competition between equally weak adsorption processes and, interestingly, it is only slightly affected by boric acid addition. The relative predominance of hydrogen or hydrolysed intermediates adsorbed at the interface can explain the step-wise change of the transient Tafel parameter $B_{\rm T}$ for not-buffered electrolytes at pH 3.2; whilst for buffered electrolytes, a linear trend is displayed by $B_{\rm T}$. The growth structure resulting from these surface conditions can be interpreted as the transition state between the biphasic fcc+hcp and the single phase hcp structure. In the presence of boric acid, the transition pH range is slightly shifted towards less acidic value.

More defined structural types are those obtained at pH values above the transition range: [11.0] and [00.1] PO, without H_3BO_3 ; and [10.0] + [11.0] mixed PO structure, with H_3BO_3 . The corresponding transient kinetic behaviour is very different.

When [11.0] texture develops, outgrowth occurs with low C_{ads} and B_T values as a consequence of stable adsorption of discharge intermediates. Outgrowth progressively decreases giving rise to lateral growth as a consequence of electrolyte ageing, due to the evolving hydrolytic speciation, and with pH increase. Mono-oriented [00.1] layers are obtained at high pH, in conditions of strong surface coverage by hydroxides or basic salts and accumulation of reducible species at

the interface, resulting in the highest C_{ads} and the lowest B_T values.

The mixed structure with [10.0] + [11.0] PO is typical of electrolytes containing boric acid. The electrokinetic behaviour drastically changes: $B_{\rm T}$ increases up to 3RT/F; $C_{\rm ads}$ slightly increases with respect to Co baths of same pH without H₃BO₃; polarisation effects appear during the transients. These changes point to different phenomena: the high $B_{\rm T}$ value can be related to adsorption or chemical contribution to the activation overvoltage; correspondingly, the pseudo-capacitance is relatively high and a pseudo-diffusional transient overvoltage is observed because of faradaic and adsorption processes overlapping. According to this interpretation, cobalt discharge takes place from complex species adsorbed at the surface; these complex species could be formed by $Co(OH)^+$ -borate or polyborates interaction, since their stability appear to increase as electrolyte acidity decreases. The highest values of both $B_{\rm T}$ and C_{ads} occur in the presence of CoCl₂ 0.1 M in the plating solution, suggesting that chloride are directly involved in the reaction mechanism stabilising discharge intermediates.

Based on these arguments, the correlation between SCP transient behaviour and the different growth structure observed in ECD Co from sulphamate solutions can be rationalised considering the stability and influence upon nucleation and growth of different surface species, whose behaviour depends on the electrolyte pH and hydrolytic equilibria. Three basic growth modes can be identified:

- 1. *Outgrowth* or perpendicular [11.0] textured growth, with transient Tafel parameter $RT/F < B_T < 3RT/2F$: hydrolysis influence is confined to the interface, where local stabilisation of intermediate hydrolysed species results in weak nucleation activity and stable growth; the surface stability of hydrolysed species is reduced by acidity increase, as shown by both B_T and C_{ads} increase. This is the growth mode characteristic of pure cobalt sulphamate solution at pH > 3.2; it is negatively affected by solution ageing, degrading towards highly defective and even amorphous growth structure but can be effectively stabilised by chloride addition.
- 2. Lateral growth, i.e. [00.1] textured growth, with $B_{\rm T} \leq RT/F$: hydrolysed species are stable in the bulk solution and surface coverage is very high; precipitation and incorporation of hydrolytic products occurs at the growing surface without hindering crystal growth; the peculiarity of these growth conditions leads to cellular crystallisation. Deposits with strong [00.1] texture are not easily obtained from not-buffered aged electrolytes at high pH unless in conditions of epitaxial growth on [1 1 1] textured Cu substrate; in this case highly [00.1] textured deposits can be obtained at pH as low as 4.
- 3. *Cluster growth*, with B_T (2.5–3) *RT/F*: this growth mode corresponds to the [10.0] + [11.0] mixed texture obtained from H₃BO₃ buffered solution at pH > 3.5. In the presence of boric acid, growth kinetics is related to the stabili-

sation of discharge intermediates as complexes stabilised at the surface by boric acid; the formation of stable nuclei requires cooperative adsorption and discharge of intermediates, resulting in complex morphological features.

The nuclei formation, dependent on the substrate or imposed by the solution, and the deposits morphology, resulting in pyramids or ridges growth, in the absence or presence of boric acid respectively, point to a specific role of boric acid in the electrocrystallisation process. In agreement with the interpretation first proposed by Simonova and Rotinyan [55] and recently, by Zech and Landolt [59], the kinetic influence of boric acid could be ascribed to surface interaction by adsorption or complex species formation.

In conclusion, the kinetics-structure relationship in cobalt electrocrystallisation from sulphamate electrolyte is demonstrated by the correlation between the transient Tafel parameter and growth structure: the highest values of $B_{\rm T}$ in the range of 3RT/F are found when layer growth proceeds by independent and continuous nucleation from solutions with boric acid; lower values are related to different processes: (1) hydrogen adsorption and evolution, when $B_{\rm T}$ is about 2RT/F, resulting in the formation of two-phase or single phase highly defective structure; (2) adsorption of stable hydrolysed species as discharging intermediates, when $B_{\rm T}$ is slightly higher than RT/F, resulting in self-perpetuating layer growth; (3) precipitation of hydroxides or basic salts at grain boundaries, when $B_{\rm T}$ is lower than RT/F, resulting in cellular crystallisation through lateral spreading of growth steps.

References

- H. Fischer, Elektrolytische Abscheidung und Elektrokristallisation von Metallen, Springer Verlag, Berlin, 1954;
 - H. Fischer, Electrodepos. Surf. Treat. 1 (1972-1973) 239;
 - H. Fischer, Ibidem 1 (1972–1973) 319.
- [2] J. Amblard, M. Froment, N. Spyrellis, Surf. Technol. 5 (1977) 205.
- [3] J. Amblard, I. Epelboin, M. Froment, G. Maurin, J. Appl. Electrochem. 9 (1979) 233.
- [4] A. Argyriou, N. Spyrellis, Trans. IMF 71 (3) (1993) 83.
- [5] H.S. Karayannis, G. Patermarakis, Electrochim. Acta 40 (1995) 1079.
- [6] T. Osaka, Electrochim. Acta 45 (2000) 3311.
- [7] S. Armyanov, Electrochim. Acta 45 (2000) 3323.
- [8] W. Hull, Phys. Rev. 17 (1926) 571.
- [9] H. Kersten, Physics 2 (1932) 274.
- [10] N.A. Pangarov, St. Rashkov, Comput. Rend. Acad. Bulgare Sci. 13 (1960) 439.
- [11] Yu.M. Polukarov, Russ. J. Phys. Chem. 34 (1960) 68.
- [12] L. Cadorna, P. Cavallotti, Electrochim. Metall. 1 (1966) 364.
- [13] R. Sard, C.D. Schwartz, R. Weil, J. Electrochem. Soc. 113 (1966) 424.
- [14] Y.N. Sadana, Surf. Technol. 5 (1977) 97.
- [15] M. Cerisier, K. Attenborough, E. Jedryka, M. Wojcik, S. Nadolski, C. Van Haesendonck, J.P. Celis, J. Appl. Phys. 89 (2001) 7083.
- [16] T.S. Eagleton, J.P.G. Farr, Trans. IMF 80 (2002) 9.
- [17] J. Dille, J. Charlier, R. Winand, J. Mater. Sci. 32 (1997) 2637.
- [18] T. Cohen-Hyams, W.D. Kaplan, J. Yahalom, Electrochem. Solid-State Lett. 5 (2002) C75.
- [19] H.L. Gaigher, N.G. Van Der Berg, Electrochim. Acta 21 (1976) 45.

- [20] S. Nakahara, S. Mahajan, J. Electrochem. Soc. 127 (1980) 283.
- [21] N.A. Pangarov, S.D. Vitkova, Electrochim. Acta 11 (1966) 1733.
- [22] N.A. Pangarov, J. Electroanal. Chem. 9 (1965) 70.
- [23] R. Breckpot, An. R. Soc. Esp. Fis. Quim. 61B (1965) 51.
- [24] S. Armyanov, S.D. Vitkova, Surf. Technol. 7 (1978) 319.
- [25] G.I. Finch, H. Wilman, L. Yang, Disc. Faraday Soc. 1 (1947) 144.
- [26] I.M. Croll, B.A. May, in: Electrodeposition Technology Theory and Practice, ECS Proc. 87-17, L.T. Romankiw, D.R. Turner (Eds.), ECS Pub., Pennington, NJ, 1987, p. 295.
- [27] M. Froment, G. Maurin, C. R. Acad. Sci. Paris 266C (1968) 1017.
- [28] H. Nakano, K. Nakahara, S. Kawano, S. Oue, T. Akiyama, H. Fukushima, J. Appl. Electrochem. 32 (2002) 43.
- [29] J. Scoyer, R. Winand, Surf. Technol. 5 (1977) 169.
- [30] A.K.N. Reddy, J. Electroanal. Chem. 6 (1963) 141;
 A.K.N. Reddy, S.R. Rajagopalan, Ibidem 36 (1963) 153;
 A.K.N. Reddy, S.R. Rajagopalan, Ibidem 6 (1963) 159.
- [31] P.L. Cavallotti, E. Galbiati, Tu Chen, in: Electroplating Engineering and Waste Recycle, D. D. Snyder, U. Landau, R. Sard (Eds.), ECS Pub., Pennington, NJ, 1983, p.130.
- [32] P. Cavallotti, G. Caironi, Surf. Technol. 7 (1978) 1.
- [33] Tu Chen, P. Cavallotti, Appl. Phys. Lett. 41 (1982) 205.
- [34] Tu Chen, P.L. Cavallotti, IEEE Trans. Magn. 18 (1982) 1125.
- [35] P.L. Cavallotti, A. Vicenzo, in: Fundamental Aspects of Electrochemical Deposition and Dissolution, M. Matlosz, D. Landolt, R. Aogaki, Y. Sato, J.B. Talbot (Eds.), PV 99-33, ECS Pub., Pennington, NJ, 2000, p. 123.
- [36] P.L. Cavallotti, A. Vicenzo, M. Bestetti, S. Franz, Surf. Coat. Technol. 169–170 (2003) 76.
- [37] G.B. Harris, Philos. Mag. 43 (1952) 113.
- [38] M.H. Mueller, W.P. Chernock, P.A. Beck, AIME Trans. 212 (1958) 39.

- [39] R. Piontelli, G. Poli, G. Serravalle, in: Transactions of the Symposium on Electrode Processes, E. Yeager (Ed.), Wiley, NY, 1959, p. 67;
 R. Piontelli, Electrochim. Metall. 1 (1966) 5.
- [40] P.L. Cavallotti, D. Colombo, U. Ducati, A. Piotti, in: Electrodeposition Technology Theory and Practice, L. Romankiw, D.A. Turner (Eds.), PV 87-17, ECS Pub., Pennington, NJ, 1987, p. 429;
 P.L. Cavallotti, B. Bozzini, L. Nobili, G. Zangari, Electrochim. Acta 39 (1994) 1123.
- [41] A. Vicenzo, P.L. Cavallotti, J. Appl. Electrochem. 32 (2002) 743.
- [42] L.O. Olikhovska, Mater. Sci. Forum 321-324 (2000) 103.
- [43] B.E. Warren, X-ray Diffraction, Dover Publications, New York, 1990.
- [44] O.S. Edwards, H. Lipson, Proc. R. Soc. 180A (1941) 268.
- [45] T.H.V. Setty, H. Wilman, Trans. Faraday Soc. 51 (1955) 984.
- [46] N.A. Pangarov, V. Velinov, Electrochim. Acta 13 (1968) 1641.
- [47] S.K. Verma, H. Wilman, J. Phys. D: Appl. Phys. 4 (1971) 1167.
- [48] J. Thevenin, J. Microsc. Spectrosc. Electron. 1 (1976) 7.
- [49] C.F. Baes, R.E. Mesmer, in: The Hydrolysis of Cations, Wiley, 1976, p. 238.
- [50] J. Ji, W.C. Cooper, Electrochim. Acta 41 (1996) 1549.
- [51] G.K. Williamson, W.H. Hall, Acta Metall. 1 (1953) 22.
- [52] I. Epelboin, M. Froment, G. Maurin, Plating 59 (1969) 1356.
- [53] J. Bard, L.R. Faulkner, in: Electrochemical Methods, Wiley, New York, 1980, p. 249.
- [54] B.E. Conway, in: Theory and Principles of Electrode Processes, The Ronald Press Company, New York, 1965, p. 236.
- [55] M.V. Simonova, A.L. Rotinyan, Zh. Prikl. Khim. SSSR 37 (1964) 1951.
- [56] K.E. Heusler, Z. Elektrochem. 66 (1962) 177.
- [57] K.E. Heusler, Ber. Bunsenges. Phys. Chem 71 (1967) 620.
- [58] F. Lenoir, R. Wiart, C.R. Acad. Sci. Paris 269C (1969) 204.
- [59] N. Zech, D. Landolt, Electrochim. Acta 45 (2000) 3461.