Effect of Manganese(II) and Boric Acid on the Electrowinning of Cobalt from Acidic Sulfate Solutions

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The effect of Mn(II) and boric acid on the electrowinning of cobalt from acidic sulfate electrolyte was investigated by electrochemical methods. The results indicated that the presence of Mn(II) or boric acid alone increased the current efficiency by 2 to 3 pct but that their combination had no additional effect. The preferred crystal orientation pattern changed from (110) (100) (101) to (100) (110) (101) in the presence of 0.1 to 10 g dm^{-3} Mn(II); an additional change, to (110) as the only preferred orientation, occurred at a very high concentration of Mn(II) (100 g dm^{-3}). Boric acid had no effect on the crystal pattern of the cobalt deposits. In general, the presence of boric acid increased the brightness of all the deposits, irrespective of the presence of Mn(II) in the electrolyte, and had no effect on the deposit morphology. The cathode polarization behavior of the cobalt electrocrystallization was affected only marginally by the presence of Mn(II) in the electrolyte, but the presence of boric acid with or without Mn(II) had a significant effect. Boric acid was found to suppress the rate of electroreduction of cobalt on stainless steel by an order of magnitude, irrespective of the presence of Mn(II).

I. INTRODUCTION

COBALT is mainly extracted as a by-product of nickel, copper, and zinc processing with the exception of a few primary arsenical ores in Morocco, Canada, and Idaho.[1] In addition to its strategic importance due to its use in magnetic alloys, in cutting and wear-resistant alloys, and in specialist chemicals and superalloys, cobalt also has high commercial value, as evidenced by its recent high price.[2,3]

About 70 pct of the world's total cobalt production is obtained from pure cobalt sulfate solutions[4] through hydrometallurgical routes, in which the final step of recovery is generally electrowinning. However, electrowinning of cobalt from sulfate baths containing additives such as Na$_2$SO$_4$, H$_3$BO$_3$, (NH$_4$)$_2$SO$_4$, and NaF is also reported in the literature.[5-8]

The presence of metal ion impurities such as Cu(II), Mn(II), Zn(II), Fe(II), Fe(III), Al(II), Mg(II), As(III), Sb(III), and Bi(III) in the electrolytic baths is known to affect the electrodeposition of cobalt.[9-16] For example, Zn(II) is reported to decrease the current efficiency (CE) by inhibiting eletrocrystallization; it shows anomalous co-deposition of zinc.[12,13] Likewise, Fe(II) affects the quality of the cobalt deposit, changes the mechanism of deposition, and inhibits the early stages of cobalt nucleation and growth.[11,14] Iron has also been reported to result in anomalous cobalt deposition, due to hydrogen evolution in the vicinity of the cathode.[15,16]

We are particularly interested in determining the effect of Mn(II), which invariably accompanies cobalt in the hydrometallurgical processing, on the characteristics of cobalt electrodeposition. Koletnikov et al.[17] have reported that the presence of manganese ion impurity adversely affects the cobalt deposit quality. Manganese also precipitates out as MnO$_2$ at the anode during the electrodeposition process.[18] In this article, we report the results of our work on the effect of Mn(II) in the range of 0.1 to 100 g dm^{-3} on the CE, deposit quality, purity, crystal orientation, and surface morphology of the electrodeposited cobalt from acidic sulfate solution in the presence and absence of boric acid. The polarization behavior of the cathode has also been studied. The exchange current density i_0 for cobalt electrodeposition on a stainless steel cathode has been calculated in order to get information on the rate of electron transfer during the electroreduction process.

II. EXPERIMENTAL

A. Rectangular Flow Cell

Cobalt electrodeposition was carried out in a rectangular flow-through cell made from Perspex (E-Plas Pty. Ltd., Belmont, WA). The cell consisted of separate cathodic and anodic compartments, each 9 × 4 × 1 cm, separated by a microporous DARAMIC* separator of 0.6-mm thickness

*DARAMIC is a trademark of Victoria, Australia.

(Figure 1). The cathode compartment contained a stainless steel cathode with a geometric area of 5 × 4 cm. Similarly, the anode compartment contained an anode made from lead-antimony (Sb, 5 pct) of the same geometric dimensions as the cathode. The two halves of the cell with the separator in between were clamped together Viton O-rings (Ludowici MPE, Kewdale, WA). The electrolyte was circulated through the two compartments by using two separate peristaltic pumps (Cole-Parmer Instrument Company, Victoria, Australia, model 7553-75). Each compartment accommodated the placement of the reference electrodes used for measuring the anode and the cathode potentials during the electrowinning experiments.

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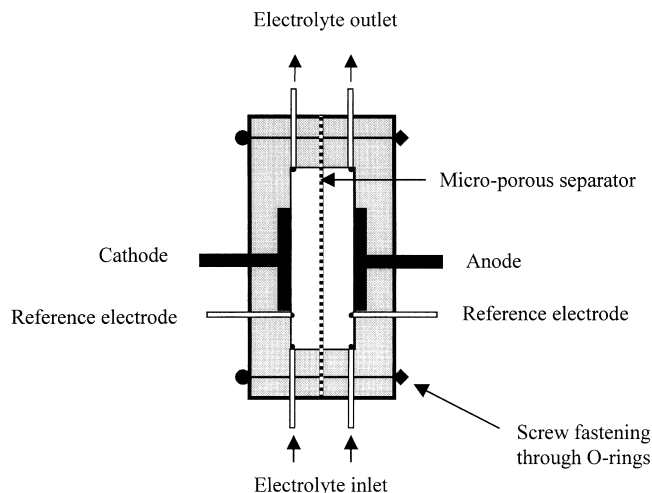Manuscript submitted October 3, 2000.

Fig. 1—Schematic drawing of the rectangular flow-through cell.

B. Reagents

Ultrapure water (Millipore Australia Pty. Ltd., NSW, Australia) was used for preparing solutions along with the following analytical grade chemicals: cobalt sulfate ($CoSO_4.6H_2O$), manganese sulfate ($MnSO_4.6H_2O$), boric acid (H_3BO_3), and sulfuric acid (H_2SO_4); all were from UNIVAR (NSW, Australia), APS Finechem.

C. Electrode Preparation

For the electrodeposition and polarization studies, the surface of the electrode prior to metal electrodeposition was polished with 400 and then 1200 grade silicon carbide paper to mirror finish and then rinsed with 1 M HCl followed by ultrapure water.

D. Electrolysis

All the electrodeposition experiments were conducted for 2 hours at a current density of 200 A m^{-2} by applying current from a regulated power supplier (0 to 30 V, 5 A, DC power supply, Dicksmith Electronics, Perth, Australia). A precision voltmeter and an ammeter were placed in the cell circuit to record the potentials and current. The flow rate of the electrolyte was maintained at 1.8 dm^3 h^{-1}. A thermostat (Grant (Selbys) Instruments, Perth, Australia) was used for maintaining the electrolyte temperature at 60 $\pm$ 1 °C. The pH of the electrolyte was kept at 3 by using dilute H_2SO_4. All potentials were measured using saturated calomel electrode (SCE) and quoted as such in this article. After electrolysis, the cathode was removed from the cell, thoroughly washed with water, and dried. The cathode CE was calculated from the weight gained by the cathode following electrolysis.

E. Polarization Measurements

All the experiments for studying the polarization behavior were carried out with 100 cm^3 electrolyte at 25 $\pm$ 1 °C. A stainless steel disk electrode 3 mm in diameter (austenitic grade 316), a platinum wire 0.5 mm in diameter, and a SCE were used as the working, auxiliary, and reference electrodes,

respectively. A PAR model 273A potentiostat/galvanostat (EG&G Instruments, Princeton, NJ, USA) was used for scanning the potential within 0 to −950 mV at a scan rate of 10 mV s^{-1}. High-purity nitrogen was used to sparge out dissolved oxygen and to maintain an inert atmosphere throughout the polarization studies. The exchange current density (i_0) value for the cobalt deposition process for each of the systems was calculated from the Tafel plots, as reported earlier.[19]

F. Deposit Examination

Sections of the cobalt electrodeposits were dissolved in nitric acid and were analyzed by inductively coupled plasma (ICP) analysis for finding out the manganese content in the cobalt deposits. A PHILIPS* PW 1050 X-ray diffractometer

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*PHILIPS is a trademark of Philips Electronic Instruments Corp., Mahwah, NJ.

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was used to examine the cobalt deposits to determine their preferred crystal orientations. The surface morphology of the deposits was examined by scanning electron microscopy (SEM) using a PHILIPS XL 20 scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

A. Cathodic Current Efficiency

Thermodynamically, the hydrogen evolution reaction is expected to interfere with the cobalt electrodeposition from acidic solutions, which lowers the CE of cobalt deposition. Thus, hydrogen evolution was kept to a minimum by maintaining the pH of the electrolyte at 3 and also by separating the catholyte from the anolyte by a microporous DARA-MIC* separator so as to restrict any transfer of H$^+$ ion from the anolyte to the catholyte.

As can be seen from the Table I, the CE of cobalt electrodeposition from pure cobalt sulphate solution was ~97 pct. The addition of Mn(II) in the range of 0.1 to 100 g dm^{-3} increased the CE by ~2 to 3 pct.

Boric acid generally acts as a brightening agent as well as a cathode polarizer for the electrodeposition of metals such as nickel.[20] Its effect on cobalt was thus investigated. The results from Table I indicate that the presence of 12 g dm^{-3} boric acid increased the CE by ~2 pct and that the addition of Mn(II) to the solution containing boric acid had virtually no effect on the CE. It can be concluded that the addition of Mn(II) and boric acid individually or together to the electrolytic bath has a beneficial effect on the CE. The CE is approximately 100 pct in the presence of these additives in the investigated concentration range, which suggests that the hydrogen evolution is almost completely suppressed. In the case of Mn(II), the co-deposition of manganese with cobalt is also a possibility. With this in mind, the purity of the electrodeposited cobalt was investigated. The analysis of the sections of the deposited metal showed that the purity of the cobalt remained at 99.99 $\pm$ 0.01 pct even at a very high concentration (100 g dm^{-3}) of Mn(II) in the electrolyte. The manganese content of the electrodeposited cobalt was found to be very small. The electrodeposited cobalt metal obtained from the electrolyte with 0.1 g dm^{-3} Mn(II) contained only 6 μg of manganese

Table I. Effect of Manganese (II) on the Electrowinning of Cobalt from Sulfate Electrolyte

[Mn(II)] (g dm^{-3})	[H$_3$BO$_3$] (g dm^{-3})	CE (Pct)	Mn(II) Oxidation as Pct of the Total Anode Reaction (Pct)	Crystal Orientation (hkl)	E_n (mV)	NOP (mV)	ΔNOP (mV)	i_0 (mA cm^{-2})
0	0	97.2	—	(110)(100)(101)	−780	−150	0	2.1×10^{-4}
0.1	0	99.5	1	(100)(110)(101)	−782	−152	−2	5.7×10^{-4}
1	0	99.8	6	(100)(110)(101)	−784	−154	−4	6.6×10^{-4}
10	0	99.9	16	(100)(110)(101)	−788	−158	−8	8.1×10^{-4}
100	0	99.5	100	(110)	−786	−156	−6	7.7×10^{-4}
0	12	99.4	—	(110)(100)(101)	−798	−168	−18	1.1×10^{-5}
0.1	12	99.3	1	(100)(110)(101)	−800	−170	−20	1.3×10^{-5}
1	12	99.7	6	(100)(110)(101)	−804	−174	−24	5.3×10^{-5}
10	12	99.7	15	(100)(110)(101)	−808	−178	−28	6.1×10^{-5}
100	12	100.0	100	(110)	−814	−184	−34	7.6×10^{-5}

per gram of the cobalt. The manganese content increased to 160 μg when the concentration of Mn(II) in the electrolyte was increased by 1000 (100 g dm^{-3}). The presence of boric acid suppressed the manganese content in the electrodeposited cobalt. For example, in the presence of 12 g dm^{-3} H$_3$BO$_3$, the manganese content of the electrodeposited cobalt metal obtained from the electrolyte containing 100 g dm^{-3} Mn(II) was only 30 μg per gram of the metal.

The precipitation of MnO$_2$ at the anode is expected when Mn(II) is present in the electrolyte according to the following reaction:

$$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$$

Black solid particles were found at the anode during the electrowinning of cobalt; they were analyzed and found to be MnO$_2$. The change in the concentration of Mn(II) in the electrolyte during each of the cobalt electrodeposition experiments was determined and the results were used to calculate the percentage of the total electrical charge that corresponded to Mn(II) oxidation to MnO$_2$. The results are listed in Table I. Clearly, the amount of charge consumed for Mn(II) oxidation at the anode is a function of the concentration of Mn(II) in the electrolyte. Only 1 pct of the charge is consumed for Mn(II) oxidation at 0.1 g dm^{-3} Mn(II) in the bath; the rest of the charge is responsible for the O$_2$ evolution. However, at a very high concentration of Mn(II) (100 g dm^{-3}) in the electrolyte, the anode reaction is almost completely Mn(II) oxidation.

B. Crystallographic Orientation

The X-ray diffraction analysis results of the cobalt electrodeposits are presented in Table I; they clearly show that Mn(II) has a significant effect on the crystal orientation of the cobalt deposits. The presence of up to 10 g dm^{-3} Mn(II) in the solution changed the preferred crystal orientation from (110) (100) (101) to (100) (110) (101) regardless of the presence of boric acid. The increase of Mn(II) concentration in the electrolyte to 100 g dm^{-3} resulted in the (110) plane being the only preferred orientation. The deposit morphology of cobalt at this high concentration of Mn(II) consisted of polyhedral crystals.

C. Deposit Morphology

Visually, all the cobalt electrodeposits obtained from acidic sulfate solutions were bright, smooth, and uniform except for the deposits obtained from the electrolytes containing 100 g dm^{-3} of Mn(II). The addition of boric acid to the electrolytes produced brighter deposits.

The SEM examination of the deposits showed that increasing the concentration of Mn(II) progressively deteriorated the quality of the deposit (Figures 2(a) through (d)). This is consistent with the findings of Koletnikov et al.[17] The cobalt deposit obtained from pure cobalt sulfate solution consisted of fibrous angular and pyramidal crystals of sizes varying from 2 to 7 μm that were oriented randomly throughout the deposit (Figure 2(a)). The addition of 0.1 g dm^{-3} Mn(II) produced elongated and mostly spindle-shaped fibrous crystals, oriented randomly, parallel to the cathode surface (Figure 2(b)). Further increases in the Mn(II) concentration did not change the shape of the crystals but decreased the size of the crystals (Figure 2(c)). At a very high concentration of Mn(II) in the electrolyte (100 g dm^{-3}), the deposit was nodular, consisting of polyhedral crystals of varying sizes (3 to 8 μm). Patches of dendritic growth also appeared (Figure 2(d)).

The addition of boric acid to the pure cobalt sulfate electrolyte resulted in sharp-edged, elongated, platelike crystals with clusters of small crystallites distributed randomly throughout the deposit (Figure 2(e)). Its effect was quite nominal when Mn(II) was also present in the electrolyte. The results were similar to those shown in Figures 2(b) through (d).

D. Polarization Behavior

Figure 3 shows the polarization (I-V) behavior of cobalt electrodeposition from pure cobalt sulfate solution on a stainless steel cathode in the presence and absence of boric acid. It is evident from the figure that hydrogen is evolved (marked "A" in Figure 3) prior to the cobalt electrodeposition, and that the presence of boric acid causes polarization, which shifts the cobalt electrodeposition to more negative potentials.

By using the procedures reported earlier,[20] the nucleation potential E_n and the crossover potential E_{co} were then determined. For each of the systems, the nucleation overpotential (NOP), which is the difference between E_n and E_{co}, was calculated and recorded in Table I. The NOP value for the electrolyte in the absence of the additives is −150 mV. The relative effects of the additives can best be seen by comparing
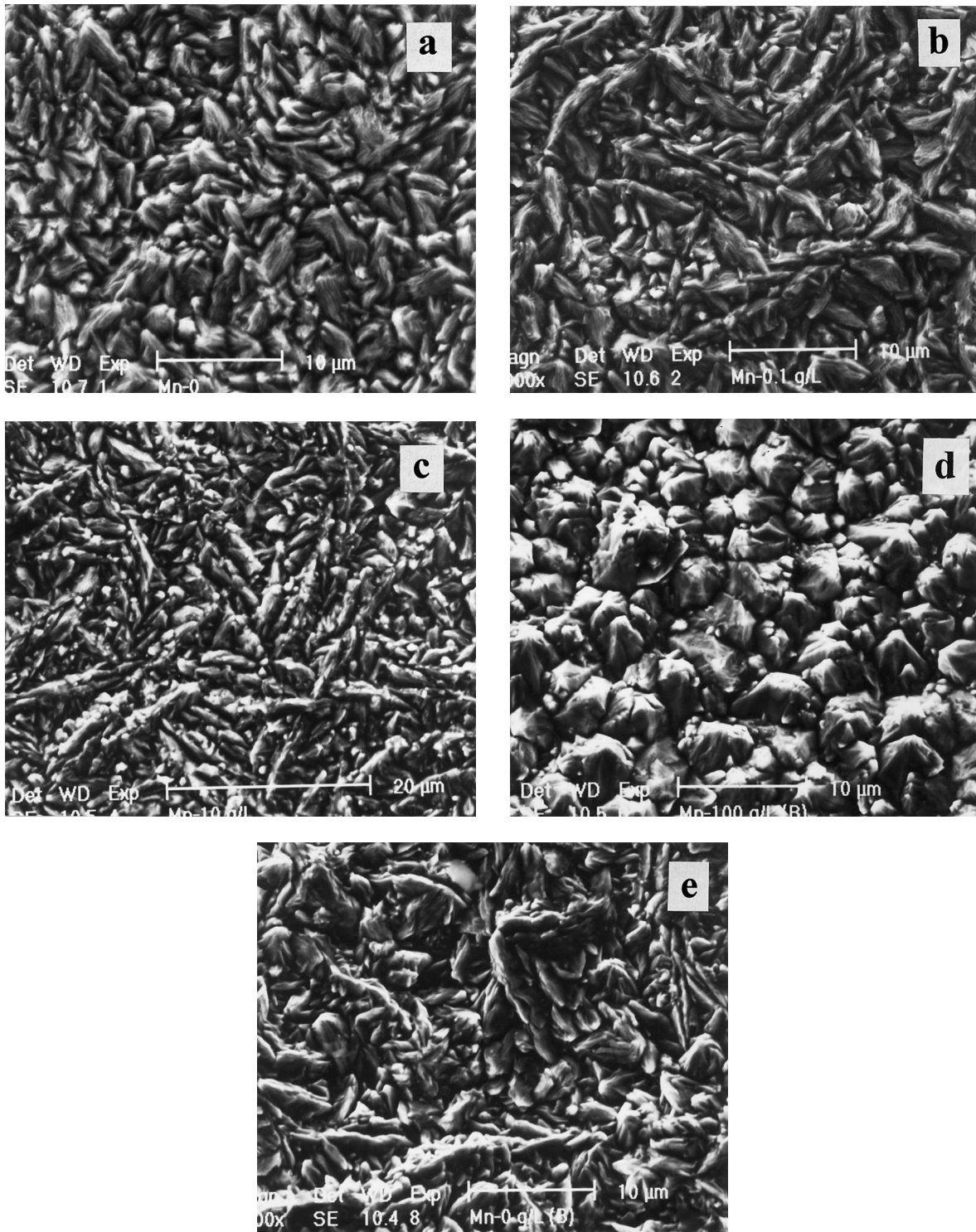
Fig. 2—SE micrograph of the cobalt deposits from sulfate electrolyte (60 g dm^{-3} cobalt, pH 3.0, and temperature 60 °C). (*a*) Pure cobalt sulfate electrolyte, (*b*) [a] + Mn(II) − 0.1 g dm^{-3}, (*c*) [a] + Mn(II) − 10 g dm^{-3}, (*d*) [a] + Mn(II) − 100 g dm^{-3}, and (*e*) [a] + H$_3$BO$_3$ − 12 g dm^{-3}.

the shift in the NOP from the baseline value of −150 mV. This shift is recorded in Table I as ΔNOP.

As can be seen from Table I, the addition of Mn(II) to the baseline electrolyte has only a marginal effect (−2 to −8 mV) on the NOP value. However, the effect of the addition of boric acid is quite significant (ΔNOP = −18 to −34 mV). This could arise from the adsorption of boric acid on the cathode surface. This is not surprising in view

of our previously reported results related to the effect of boric acid on nickel electrodeposition.[20] The effect of the co-addition of Mn(II) and boric acid on the NOP is generally dominated by boric acid. Increasing the concentration of Mn(II) from 0.1 to 100 g dm^{-3} in the presence of 12 g dm^{-3} of boric acid shifts the ΔNOP value progressively more negatively (Table I). Thus, the presence of boric acid together with Mn(II) polarizes the cobalt deposition process quite
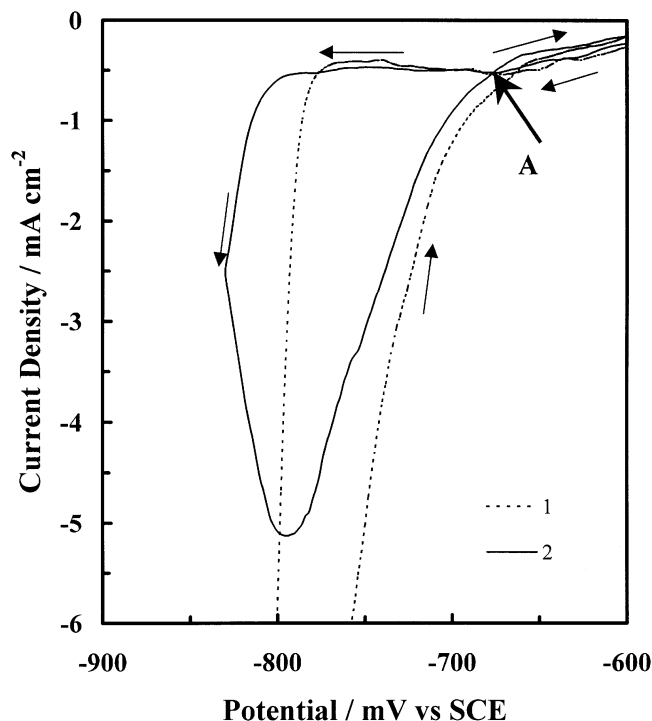
Fig. 3—Cyclic voltammograms of cobalt sulfate electrolyte. (1) Pure cobalt sulfate electrolyte and (2) [1] + H_3BO_3 − 12 g dm^{-3}.

significantly. The mechanism of this effect is not clear at this stage.

The exchange current density, the i_0 value data noted in Table I, indicates that boric acid certainly suppresses the rate of electron transfer of the electroreduction of cobalt on stainless steel irrespective of the presence of Mn(II) in the electrolyte. The values change from $5.0 \pm 0.5 \times 10^{-4}$ mA cm^{-2} to $6.0 \pm 0.5 \times 10^{-5}$ mA cm^{-2} when boric acid is added to the solution, which indicates that the presence of boric acid reduces the rate of electron transfer by an order of magnitude.

IV. CONCLUSIONS

1. The presence of Mn(II) in the electrolyte up to 100 g dm^{-3} does not affect the purity of the cobalt electrodeposits. However, the CE is increased marginally (2 to 3 pct).
2. The presence of boric acid produces brighter looking deposits, but no definitive correlation between the surface morphology and crystal orientation of the deposited metal is evident.
3. Boric acid increases the NOP of cobalt and shifts the electrodeposition of cobalt to more negative potentials.
4. Mn(II) is oxidized to MnO_2 at the anode in the electrolytic cell. The proportion of the anodic current corresponding to this oxidation is very low with 0.1 g dm^{-3} Mn(II) but increases with increasing concentration of Mn(II) in the electrolytic bath.

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