Nickel and cobalt synergism effect in zinc electrowinning from sulphate electrolytes

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An investigation has been made on the mechanism and kinetics of the electrochemical processes occurring during zinc electrowinning from sulphuric acid electrolytes containing Ni^{2+}, Co^{2+} and mixtures of the two impurities. The electrochemical nature of the "synergism" effect manifested by the common action of these two metal impurities has been established. It has been demonstrated that as a result of specific adsorption of $(Co(SO_4))^{(2n-2)-}$ anions onto the zinc electrode, the partial discharge rate of Ni^{2+} is catalyzed, leading to an increase of its bulk content in the zinc deposits.

1. Introduction

Two fundamental problems involved in the production of zinc by electrowinning from sulphuric acid electrolytes are the consumption of electric power per unit weight of metal obtained and the structure of the zinc deposit. Both problems are determined by the presence in the working electrolytes of metallic impurities that are more electropositive than zinc, such as: Ni, CoFe, Cu, As, Sb, and Ge. These impurities affect zinc electrowinning deleteriously by accelerating the parallel process of hydrogen evolution due to the lower overvoltage for the discharge of H_3O^+(Ni, Co, Cu) or due to the formation of unstable hydrides with Sb, Ge, and As [1–21].

Despite the large number of studies on the negative influence of these impurities, the explanation of the mechanism of their negative action has not been completely explained from an electrochemical point of view.

In our opinion the following impurity effects have not been fully explained:

(i) The physical nature of the so-called "induction period" resulting from the action of the metal impurities of the Fe-group [1–15].
(ii) The nature of the processes leading to the so-called "synergism" effect manifested by the common action of several impurities in the electrolyte [7, 8, 10, 22–24].
(iii) The nature of the so-called "kinetic restrictions" on the partial current of codeposition of metal impurities with zinc [10, 12, 25, 26].

Although an acceptable physical model, based on the concept of the action of local galvanic couples generating hydrogen bubbles, has been developed to explain the nature of the "induction period" [19, 20, 27–29], the nature of the "synergism" effect and the "kinetic restrictions" on impurity codeposition have not been fully explained despite the large number of studies published to date [7, 8, 12, 22–26].

There are several studies [30–33] on the common action of Ni and Co in electrolytes for zinc deposition, where the aim has been to obtain double or triple alloys with zinc, thus requiring fairly high concentrations (20–50 mg dm^{-3}). It has also been established that on an equal concentration basis more nickel than cobalt is deposited with zinc [34, 35]. Akiyama and co-authors [25, 31, 36] have reported that the anomalous codeposition of Zn with Co, which generally appears in the electrodeposition of Zn-alloys with iron-group metals from the low acidity sulphate bath, also occurs in high acidity Zn electrowinning baths. It was also established by the same authors that the codeposition rates of iron-group metals with zinc differs greatly from those of other impurities (Cu, Cd, Ag) and is extremely low in the current density range employed. An analogous conclusion follows from other studies [14, 37] where it has been established that the deposition of nickel, like the other iron-based metals, is hindered by zinc ions.

This paper presents results obtained on the "synergism" effect appearing in the electrowinning of zinc from sulphuric acid electrolytes containing admixtures of Ni^{2+} and Co^{2+} in concentrations of up to 10 mg dm^{-3}, with the aim of ascertaining the physical nature of the process causing the "synergism" effect.

2. Experimental details

The experiments were carried out in a thermostatic three electrode cell in an argon atmosphere. "Reidel" (Cat. No. 11003) aluminium electrodes with surface area of 1 cm^2 were used as cathodes. They contained 0.2% Fe [19]. The anode used was platinum mesh with surface area of 100 cm^2 situated coaxially around the cathode and the reference electrode was a Hg/Hg_2SO_4 saturated electrode.

The working electrolytes were at $T = 37°C$ and pH 0.2 and had the following composition: 130 g dm^{-3}

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H_2SO_4, $15.4\,g\,dm^{-3}$ $MnSO_4 \cdot H_2O$, $220\,g\,dm^{-3}$ $ZnSO_4$ $\cdot 7\,H_2O$. Added to this electrolyte, which we shall conventionally refer to as the supporting electrolyte, were various concentrations of $NiSO_4 \cdot 7\,H_2O$ and $CoSO_4 \cdot 7\,H_2O$, so that the concentration of the metal ions from Ni and Co separately or jointly in the solution were: $Me^{2+} = 2,4,6,8,10\,mg\,dm^{-3}$. All salts used were products of Merck.

The morphology of the zinc deposits obtained at a current density of $50\,mA\,cm^{-2}$ was investigated by scanning electron microscopy (SEM) by the use of a JEOL-Superprobe 733 unit, while the concentration of the codeposited impurities were investigated by atomic-absorption analysis (Perkin Elmer), after dissolution of the zinc deposits in HNO_3.

The change of the partial rates of the parallel processes of hydrogen evolution and zinc deposition were determined by volumetric measurement of the volume of the hydrogen released, which was measured continuously in a burette with a glass bell situated above the cathode [20, 27].

The electrochemical measurements on the mechanism of the initial stages of zinc deposition were carried out by using cyclic voltammetry at scan rates of $W = 1$–$5\,mV\,s^{-1}$. For measuring the capacity of the electrode double layer the method of the so-called "isoelectric" variation of the potential was used, involving oscillographic recording of the potential transient immediately ($t = 0$–$100\,ms$) after switching-off the current in the circuit. The potential transients were recorded with a storage oscilloscope (TEK-TRONIX-5111) with differential amplifier (5A22N).

3. Experimental results and discussion

3.1. Volumetric and morphological investigations

Figures 1–3 show the change in the current efficiency for HER with the time of electrolysis (t), recorded in electrolytes containing concentrations of nickel (Fig. 1), cobalt (Fig. 2), and mixture of the two impurities (Fig. 3). It may be seen that, whereas the presence of nickel in concentrations of up to $2\,mg\,dm^{-3}$ (Fig. 1,
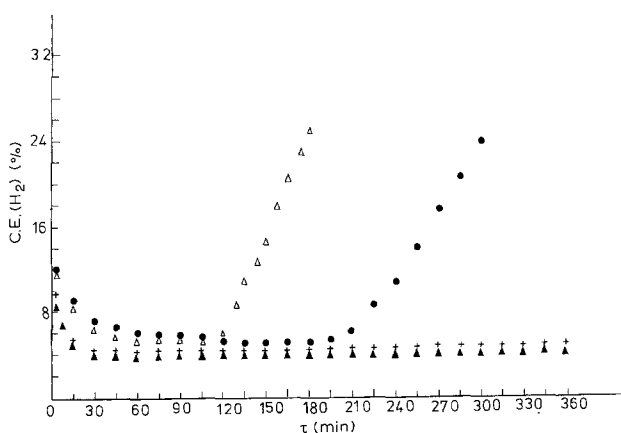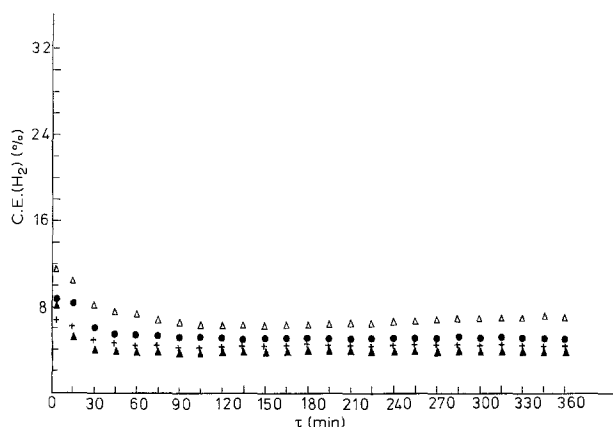
Fig. 2. Time dependence of the current yield of HER established in: (▲) supporting electrolyte; (+) supporting electrolyte with $2\,mg\,dm^{-3}\,Co^{2+}$; (●) supporting electrolyte with $6\,mg\,dm^{-3}\,Co^{2+}$; and (△) supporting electrolyte with $8\,mg\,dm^{-3}\,Co^{2+}$.

curve 2) causes almost no change in the partial rate of the HER compared to the rate measured in a supporting electrolyte (Fig. 1, curve 1), at higher nickel concentrations there is a sharp increase in the volume of the hydrogen evolved over 180 min at $6\,mg\,dm^{-3}\,Ni^{2+}$ (curve 3), or after 120 min at $8\,mg\,dm^{-3}\,Ni^{2+}$ (curve 4). This time interval preceding the sharp rise in the rate of the HER is known in the literature as the "induction" period, during which the zinc deposits are uniform, light and with good adhesion to the cathode. The "induction" period is followed by abundant hydrogen evolution (Fig. 1, curves 3 and 4), accompanied by a process of spontaneous dissolution of the deposited zinc. This is known as the "self-dissolution" stage for which a physical model has been proposed [19, 20, 27–29].

The SEM micrographs of the surface of the zinc deposits electrowon from the supporting electrolyte (Fig. 4a, b) and from electrolyte containing $6\,mg\,dm^{-3}\,Ni^{2+}$ (Fig. 5a, b) clearly indicate that nickel increases the number of pitting defects per unit area (Fig. 5a) and decreases the average size of the zinc crystallites (Fig. 5b) — a fact also established in the course of other studies [5, 7, 8, 12].
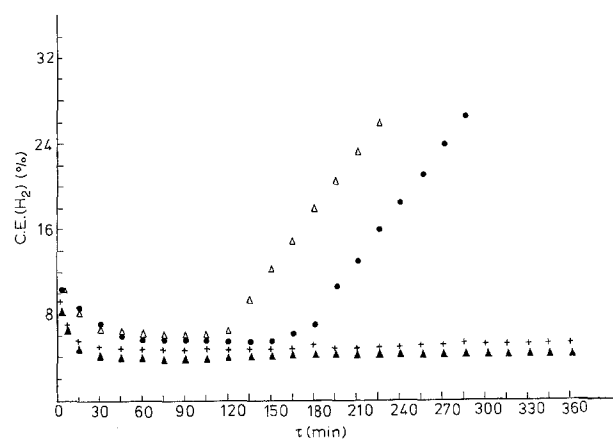
Fig. 1. Time dependence of the current yield of HER established in: (▲) supporting electrolyte; (+) supporting electrolyte with $2\,mg\,dm^{-3}\,Ni^{2+}$; (●) supporting electrolyte with $6\,mg\,dm^{-3}\,Ni^{2+}$; and (△) supporting electrolyte with $8\,mg\,dm^{-3}\,Ni^{2+}$.

Fig. 3. Time dependence of the current yield of HER established in: (▲) supporting electrolyte; (+) supporting electrolyte with $1\,mg\,dm^{-3}\,Ni^{2+}$ and $1\,mg\,dm^{-3}\,Co^{2+}$; (●) supporting electrolyte with $3\,mg\,dm^{-3}\,Ni^{2+}$ and $3\,mg\,dm^{-3}\,Co^{2+}$; and (△) supporting electrolyte with $4\,mg\,dm^{-3}\,Ni^{2+}$ and $4\,mg\,dm^{-3}\,Co^{2+}$.
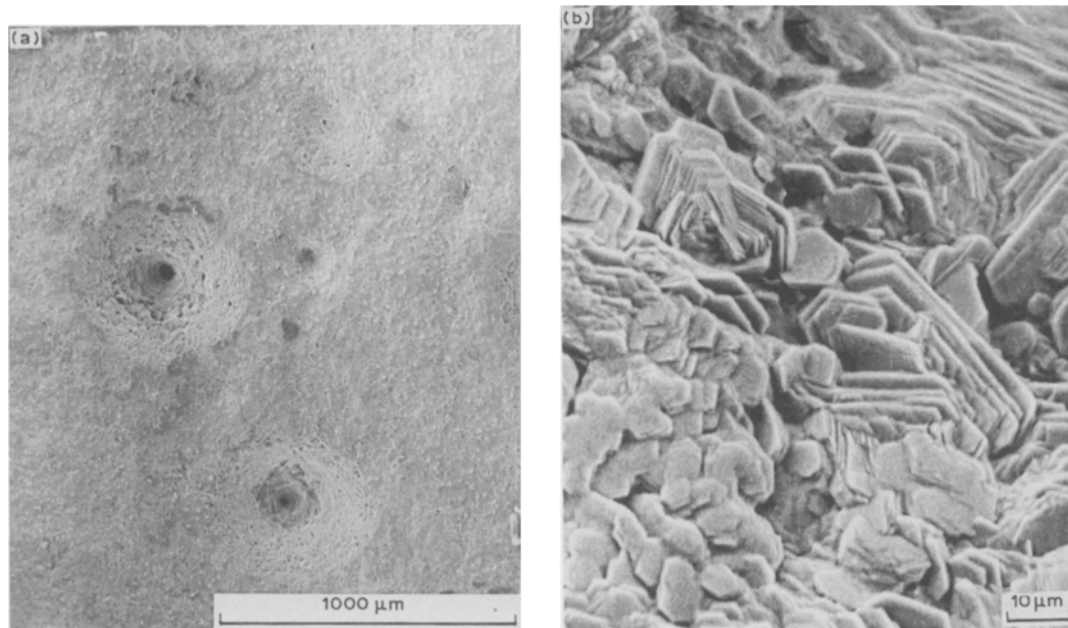
Fig. 4. SEM micrographs of zinc deposit obtained form a supporting electrolyte.

Analogous investigations were carried out in electrolytes containing various cobalt concentrations which, unlike nickel, in the investigated concentrations up to $8\,mg\,dm^{-3}\,Co^{2+}$ does not essentially change either the rate of the HER (Fig. 2) or the structure and morphology of the zinc deposits (Fig. 6a, b) — a result also established in the course of other studies [8, 38].

From the data obtained up to now it follows conclusively that these two metal impurities, when present separately in the electrolytes, show completely different activities in relation to the rate of the HER. This effect is unexpected due to the similar electrochemical behaviour of the two metals (Co and Ni) with respect to hydrogen evolution, i.e., approximately the same exchange current and Tafel coefficients [39].

The results showing the effect of the joint action of nickel and cobalt in the electrolyte on the current efficiency for the HER and on the structure of the zinc deposits are shown in Fig. 3 and Fig. 7a, b, respectively. A comparison of the results shows almost quantitatively and within the experimental error, that the negative action of the combination of $3\,mg\,dm^{-3}\,Ni^{2+}$ and $3\,mg\,dm^{-3}\,Co^{2+}$ (Fig. 3, curve 3) is equal to that observed for $6\,mg\,dm^{-3}\,Ni^{2+}$ (Fig. 1, curve 3). The same is also true for the combination of $4\,mg\,dm^{-3}\,Ni^{2+}$ with $4\,mg\,dm^{-3}\,Co^{2+}$ (Fig. 3, curve 4), compared to the action of $8\,mg\,dm^{-3}\,Ni^{2+}$.

The accelerated negative action of nickel is also observed at non-equivalent concentration ratios, i.e., mixture of $4\,mg\,dm^{-3}\,Ni^{2+}$ with $2\,mg\,dm^{-3}\,Co^{2+}$ acts as $6\,mg\,dm^{-3}\,Ni^{2+}$, while a mixture of $5\,mg\,dm^{-3}\,Ni^{2+}$
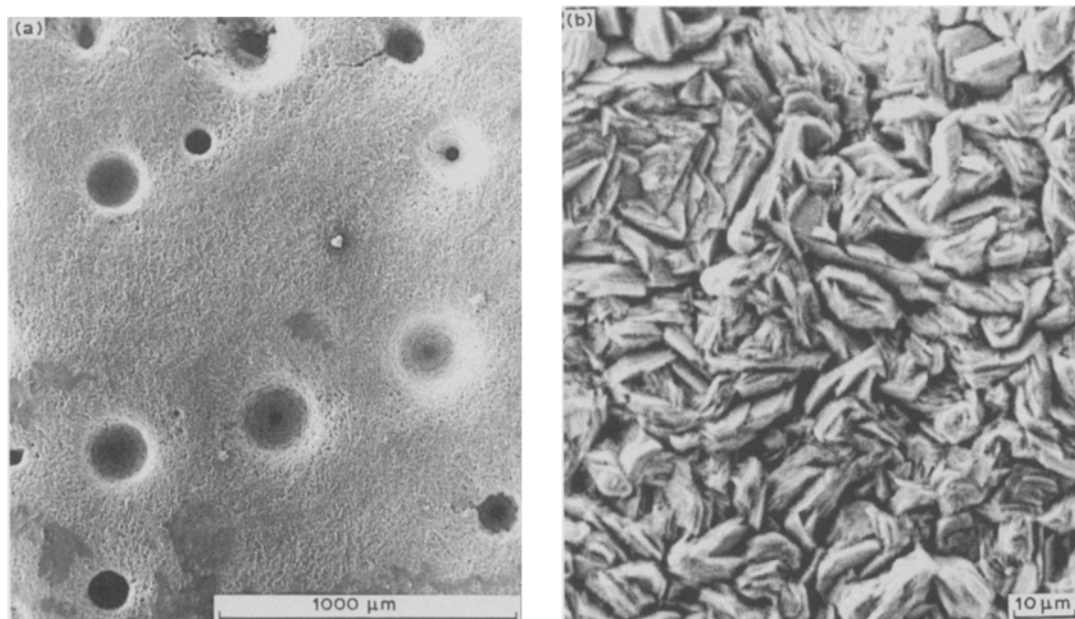

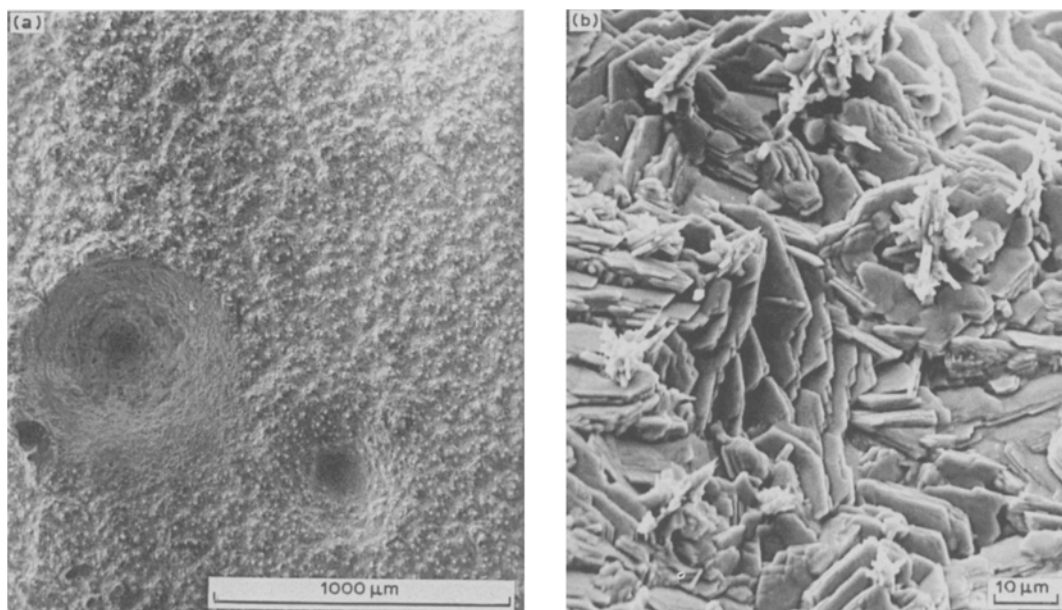Fig. 5. SEM micrographs of a zinc deposit obtained from a supporting electrolyte containing $6\,mg\,dm^{-3}\,Ni^{2+}$.

Fig. 6. SEM micrographs of a zinc deposit obtained from a supporting electrolyte containing $6 \, mg \, dm^{-3} \, Co^{2+}$.

with $3 \, mg \, dm^{-3} \, Co^{2+}$ acts as $8 \, mg \, dm^{-3} \, Ni^{2+}$. The impression is created that, in the presence of Ni^{2+} in the solution, Co^{2+} acts analogously to the Ni^{2+} ions, i.e., they contribute additively to the negative effect of the nickel. This has also been confirmed by the morphological investigations on the structure of the zinc deposits (Fig. 7a, b). Consequently, it may be asserted in the investigated case that the so-called effect of "synergism" occurs in the common action of the two ions.

Keeping in mind the fact that the negative action of the impurities is proportional to their amount codeposited with zinc [4, 5–8, 10, 13, 15] all Zn deposits were dissolved in nitric acid and analyzed by atomic-adsorption spectrophotometry. It is concluded from the results presented in Table 1, that:

1. Increasing the bulk concentration of nickel in an electrolyte containing only nickel, leads to a proportional increase in the weight of nickel codeposited with zinc. However, it is difficult to explain the fact that the amount of codeposited nickel (micrograms) is smaller by two orders of magnitude than the expected amount (mg) which should have deposited under the diffusion-limited current, based on the bulk concentration of the nickel ions. That is to say, there are so-called "kinetic restrictions" [10, 12, 25, 26] on the partial rate of codeposition of the admixture metal.

2. Particularly strange is the fact that the zinc deposits obtained from electrolytes containing only cobalt as impurity do not contain codeposited cobalt. This readily explains the independence of the current efficiency of HER on the bulk concentration of cobalt (Fig. 2).
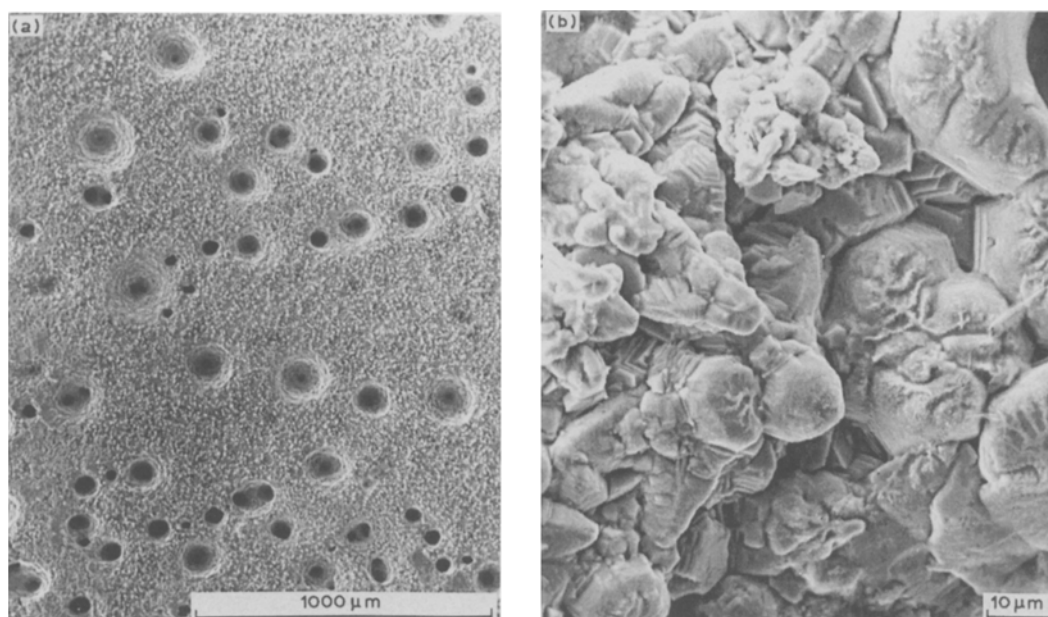

Fig. 7. SEM micrographs of a zinc deposit obtained from a supporting electrolyte containing both $3 \, mg \, dm^{-3} \, Ni^{2+}$ and $3 \, mg \, dm^{-3} \, Co^{2+}$.

3. The results obtained for zinc deposits electrowon from electrolyte containing both Ni^{2+} and Co^{2+} ions show that cobalt is not codeposited with zinc, but that the amount of nickel codeposited with zinc was increased. In the presence of cobalt the discharge of nickel on the zinc has been rendered easier. Thus from an electrolyte containing only $3\,mg\,dm^{-3}\,Ni^{2+}$ the amount of nickel codeposited with the zinc is about 2.4×10^{-6} g, whereas from an electrolyte containing $3\,mg\,dm^{-3}\,Ni^{2+}$ and $3\,mg\,dm^{-3}\,Co^{2+}$ the amount of nickel codeposited is 2.5×10^{-5} g, i.e., one order of magnitude higher. It is the same for electolyte containing only $4\,mg\,dm^{-3}\,Ni^{2+}$ with the electrolyte containing both $4\,mg\,dm^{-3}\,Ni^{2+}$ and $4\,mg\,dm^{-3}\,Co^{2+}$.

The very important conclusion to be drawn from these results is that the effect of "synergism" is caused by the higher concentration of the nickel codeposited with the zinc.

In our opinion this is a quantitative definition of the "synergism" effect, which still offers no explanation for it. It is necessary to explain how Co^{2+} facilitates the discharge stage of nickel ions. To that end we carried out kinetic investigations on the rate and mechanism of the initial stages of zinc deposition using cyclic voltammetry.

3.2. Cyclic voltammetry

Cyclic voltammetry has been employed in a large number of investigations on the electrowinning of zinc [4, 8, 9, 14, 17]. On the basis of this method, in earlier publications [19, 28] we determined the sequence and the rate of the processes taking place during the initial stages of zinc deposition on aluminium cathodes (Fig. 8). It was demonstrated that the current maximum (II) at $1.42\,V$ (curve 2) both in the former and reverse scans, is a result of the cathodic discharge of hydrogen ions on aggregates of Fe-alloying element in the aluminium substrate. The current measured at these potentials is weaker than the current obtained in free electrolyte (curve 1), as a result of underpotential deposition of a sub-monolayer of zinc over these iron aggregates [40]. This maximum does not appear

Table 1. Atomic absorption analysis of zinc deposits obtained in different electrolytes

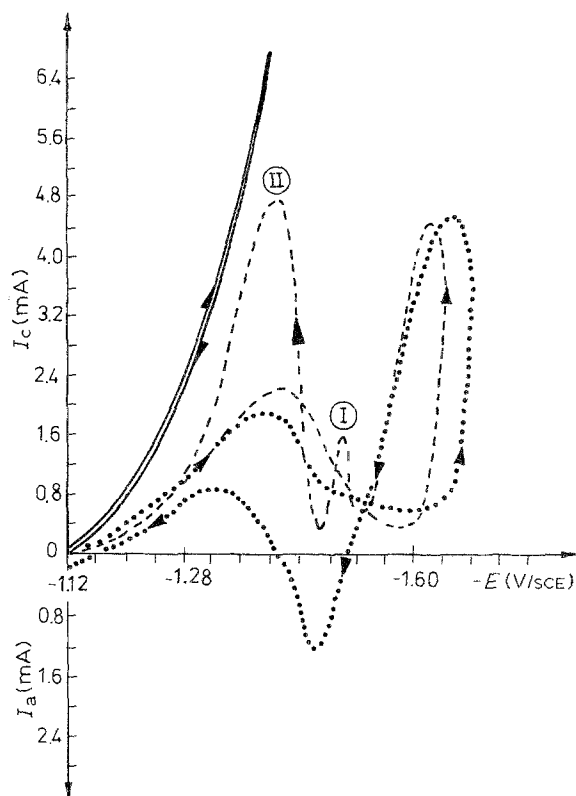| Electrolyte H_2SO_4, $MnSO_4$, $ZnSO_4$ containing		Quantity Ni and Co per $1\,(g)$ deposited-Zn	
Ni^{2+} $(mg\,dm^{-3})$	Co^{2+} $(mg\,dm^{-3})$	$Ni\,(g)$	$Co\,(g)$
–	–	2.72×10^{-6}	–
4	–	2.99×10^{-5}	–
6	–	5.84×10^{-5}	–
8	–	7.76×10^{-5}	–
–	4	1.93×10^{-6}	–
–	6	1.91×10^{-6}	–
–	8	1.92×10^{-6}	traces
2	2	1.80×10^{-6}	–
3	3	2.50×10^{-5}	–
4	4	4.18×10^{-5}	–

Fig. 8. Cyclic voltammograms traced at sweep rate $W = 5\,mVs^{-1}$ in: free of zinc supporting electrolyte (———); supporting electrolyte (·····); and supporting electrolyte with $10\,mg\,dm^{-3}\,Ni^{2+}$ (– – – –).

when the experiment is carried out on spectral-pure aluminium.

The appearance of the first zinc nuclei at $E = -1.6\,V$ leads to the so-called positive current hysteresis as a result of increased geometrical surface of the growing zinc crystallites [41] (Fig. 9). The dependance of the current on the potential, as recorded in the presence of nickel ions in the solution (Fig. 8, curve 3), shows additionally a new cathode maximum (I) recorded in the anodic part of the scan, as well as an enhanced current maximum (II).

On the basis of these current dependencies it is possible to record the degree of influence of the cobalt ions on the rate of discharge of nickel ions. The results are shown in Fig. 10 according to which, in an electrolyte containing only cobalt ($8\,mg\,dm^{-3}$), the current dependence coincides with that obtained for the supporting electrolyte, i.e., Co^{2+} does not participate in the cathode process and is not discharged on aluminium or on zinc, at the investigated concentration. This is in very good agreement with the results obtained in the previous section (Fig. 2 and Table 1). On the other hand, the current dependence obtained from solutions containing $4\,mg\,dm^{-3}\,Ni^{2+}$ and $4\,mg\,dm^{-3}\,Co^{2+}$ is almost equal to that obtained in the presence of $8\,mg\,dm^{-3}\,Ni^{2+}$, which proves conclusively that cobalt has a catalytic effect on the discharge rate of nickel on both zinc and on the Fe-aggregates. This catalytic effect of Co^{2+} on the partial discharge rate of Ni^{2+} is a new interpretation of the nature of the "synergism" effect, and it follows that this effect is of a purely electrochemical nature, i.e., this is obviously a case of electrocatalysis.
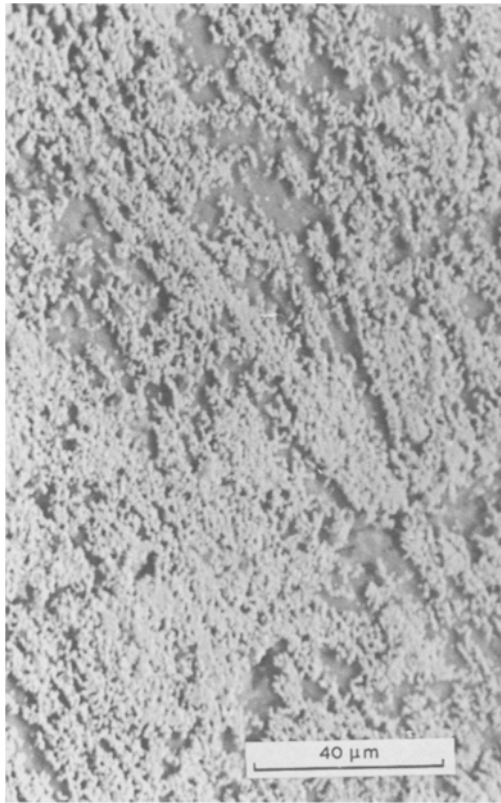
Fig. 9. SEM micrograph of a zinc deposit obtained from a supporting electrolyte at $i = 50\,mA\,cm^{-2}$ and deposition time $t = 30\,s$.

However, the question now remains, as to the stage of the general reaction of Ni^{2+} discharge at which this catalysis takes place. Measurements were carried out on the capacity of the electrode double layer during zinc deposition in solutions containing nickel, cobalt and a mixture of the two impurities.

3.3. Double-layer investigations

Pulse-type galvanostatic methods are extensively applied in studies on the mechanism of electrochemical processes and on the structure of the double layer at the electrolyte-electrode interface [42]. The poten-

tial transient obtained upon switching-on or switching-off the current must be described by a suitable kinetic equation depending on the nature of the electrochemical process [43, 44].

The so-called "isoelectric" method, i.e., the method of interrupting the current, has found extensive application particularly in systems in which the object of the investigation is the mechanism of irreversible electrochemical reactions obeying the Tafel equation [45]. This advantage also stems from the fact that, after current interruption, the measured double layer capacity is a quantitative characteristic of the electrode surface state at the moment before switching-off the current. The equations used in processing the potential transients are well known and have been described in a number of publications [42–49].

$$\eta_{st.} = a + b\,\ln i_{st}\qquad(1)$$

$$\Delta\eta = \eta_{st.} - \eta_t = b\,\ln\left(\frac{i_{st}t}{bC_{dl}} + 1\right)\qquad(2)$$

for:

$$\frac{i_{st}t}{bC_{dl}} \ll 1;\qquad \Delta\eta = \frac{i_{st}}{C_{dl}}\,t\qquad(3)$$

$$C_{dl} \approx i_{st}\left(\frac{dt}{d\eta}\right)_{t\to 0}\qquad(4)$$

where a, b are Tafel constants, η_{st} is the electrode overpotential, i_{st} is the current before switch-off, and C_{dl} is the double layer capacity.

The experiments were carried out at two current densities: $i = 50\,mA\,cm^{-2}$ and $i = 25\,mA\,cm^{-2}$, the results for (C_{dl}) being averaged values from five measurements in the time interval $t = 0–60\,\mu s$ after switching-off the current — these values are given in Table 2. The potential transients were photographed at different time intervals (Fig. 11a, b, c, d) which reveals that their gradient is no longer linear and changes when the times are longer than $100\,\mu s$ due to a pseudo capacitance effect (Fig. 11b). As established for irreversible electrochemical reactions, in such cases the time dependence becomes a logarithmic and at longer times it is deter-
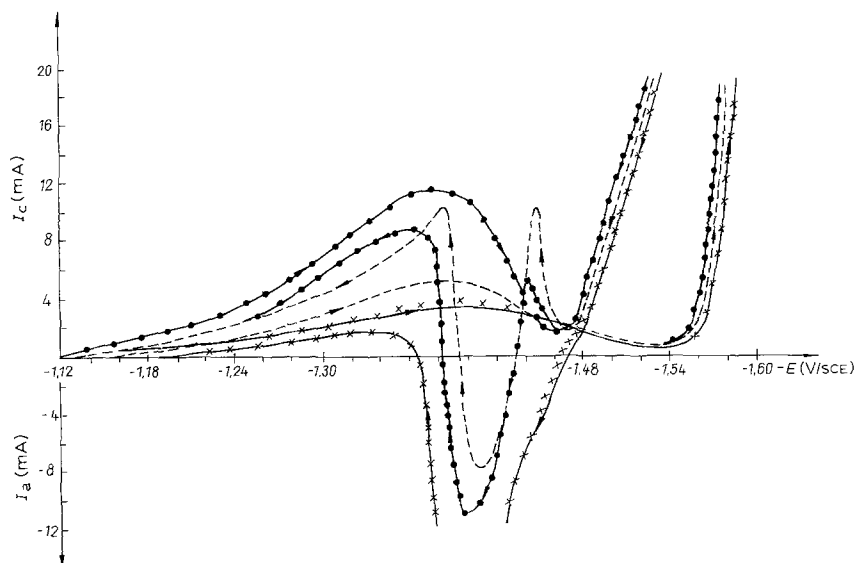

Fig. 10. Cyclic voltammograms traced at a sweep rate $W = 5\,mV$ in: supporting electrolyte (———): supporting electrolyte with $8\,mg\,dm^{-3}\,Ni^{2+}$ (————); supporting electrolyte with $8\,mg\,dm^{-3}\,Co^{2+}$ (×××××××); and supporting electrolyte with $4\,mg\,dm^{-3}\,Ni^{2+}$ and $4\,mg\,dm^{-3}\,Co^{2+}$ (······).
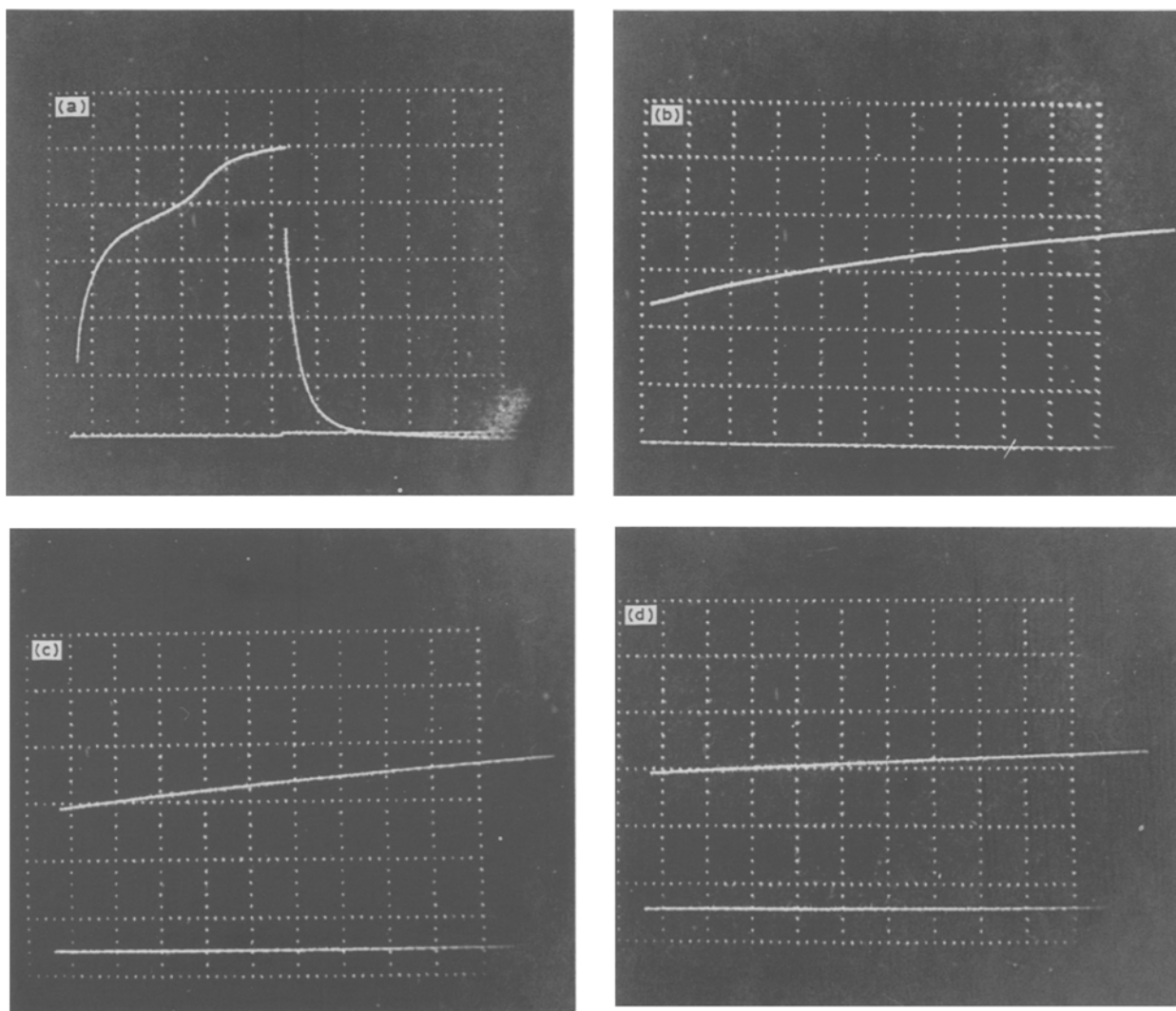
Fig. 11. Potential-time transients recorded after switching-off the current $i = 50\,\mathrm{mA\,cm^{-2}}$ at different time intervals: (a) div. Y = 100 mV, div. X = 1 ms; supporting electrolyte; (b) div. Y = 50 mV, div. X = $50\,\mu s$; supporting electrolyte; (c) div. Y = 50 mV, div. X = $20\,\mu s$ — supporting electrolyte with $8\,\mathrm{mg\,dm^{-3}\,Ni^{2+}}$; and (d) div. Y = 50 mV, div. X = $20\,\mu s$ — supporting electrolyte with $8\,\mathrm{mg\,dm^{-3}\,Co^{2+}}$.

mined by the so-called "transitional" time (Fig. 11a), proportional to the surface concentration of the depolarizer. The same type of potential transients have also been obtained by other authors in investigations of the electrochemical behavior of zinc electrodes [50], the potential delay (Fig. 11a) being interpreted as a result of ionization of discharged hydrogen atoms.

Table 2. Capacity of electrode double layer measured in different electrolytes

Electrolyte composition — $(g\,dm^{-3})$ No $ZnSO_4 \cdot 7H_2O\text{-}220;\ MnSO_4 \cdot H_2O\text{-}15.5$	$C_{dl}/\mu F\,cm^{-2}$
1. $H_2SO_4\text{-}130$	17.16 ± 1.32
2. $H_2SO_4\text{-}130;\ Ni^{2+}\text{-}10\,mg\,dm^{-3}$	16.23 ± 0.84
3. $H_2SO_4\text{-}130;\ Co^{2+}\text{-}10\,mg\,dm^{-3}$	32.46 ± 1.22
4. $H_2SO_4\text{-}130;\ Ni^{2+}\text{-}10\,mg\,dm^{-3};$ $Co^{2+}\text{-}10\,mg\,dm^{-3}$	27.22 ± 0.75
5. $H_2SO_4\text{-}35;\ Co^{2+}\text{-}10\,mg\,dm^{-3}$	24.17 ± 2.05
6. $H_2SO_4\text{-}35;\ Co^{2+}\text{-}20\,mg\,dm^{-3}$	30.05 ± 1.10
7. $H_2SO_4\text{-}260;\ Co^{2+}\text{-}10\,mg\,dm^{-3}$	38.23 ± 0.54
8. $H_2SO_4\text{-}260;\ Co^{2+}\text{-}20\,mg\,dm^{-3}$	37.42 ± 0.22

Examination of these results (Table 2 and Fig. 11) leads to the following conclusions:

1. The capacity of the double layer is approximately the same in a supporting electrolyte and in the presence of only Ni^{2+}, $C_{dl} = 15\text{–}19\,\mu F\,cm^{-2}$ (Fig. 11c) and it coincides with the values of C_{dl} measured in cationic solutions [45–49].

2. The capacity of the electrode double layer is higher by about 60% in the presence of Co^{2+} in the electrolyte and by about 40% in solutions containing both Ni^{2+} and Co^{2+}, compared to the solution free of Co^{2+} (Fig. 11d).

3. The capacity of the electrode double layer, measured in the solutions containing only Co^{2+}, increases with increasing cobalt and H_2SO_4 concentrations.

In our opinion the only reasonable explanation of the results obtained is based on the assumption that Co^{2+} ions specifically adsorb on the electrode surface. A detailed survey of the literature shows that, on the one hand, a stronger negative influence of Co^{2+} has repeatedly been established with increase in the con-

centration of H_2SO_4 [10, 51, 52], while on the other hand incorporation of Co in the anode has also been established [53, 54]. This has provided grounds for some authors [10, 55, 56] to assume the existence of cobalt complexes of the type: $(Co(SO_4)_n)^{(2n-2)-}$ in strong sulphuric-acid electrolytes, whose concentration depends on the concentration of Co^{2+} and SO_4^{2-} [57, 58].

As is known from classical work on the electrode double layer [43–49], the specific adsorption of anions leads to a decrease in the thickness of the inner Helmholz double layer, due to the stronger polarizability of the anion, and accordingly to the increase in its capacity. The values of C_{dl} measured in the presence of different anions (I^-, Cl^-, SO_4^{2-}, NO_3^-) are of the order of $35–45\,\mu F\,cm^{-2}$ [43–49], consequently there is a good agreement with the values measured here in solutions containing Co^{2+} (Table 2). The results obtained here may be consistently interpreted in terms of specific ionic adsorption of Co^{2+} on the cathode.

Consequently, the "synergism" effect manifested in catalyzing the negative influence of Ni^{2+} and Co^{2+}, is a result of specific adsorption of cobalt complexes, which due to their negative charge, facilitate the discharge of Ni^{2+} and, as a result, lead to an increase in the nickel codeposited with the zinc.

4. Conclusion

Using detailed volumetric, structural, kinetic and double layer investigations on the mechanism of zinc electrowinning from sulphuric acid electrolytes containing Ni^{2+}, Co^{2+} and combinations of the two impurities, the electrochemical nature of the "synergism" effect arising during the common action of Ni^{2+} and Co^{2+} in the working electrolytes, has been established for the first time. This "synergism" effect is probably due to the specific adsorption of cobalt anions $(Co(SO_4)_n)^{(2n-2)-}$ on the negatively charged zinc electrode, which facilitates the discharge of Ni^{2+}, i.e., catalyzes the partial rate of nickel codeposition with zinc.

Acknowledgements

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