The effect of nickel on the mechanism of the initial stages of zinc electrowinning from sulphate electrolytes. Part I. Investigations on a spectrally pure aluminium cathode

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The effect of nickel ions on the mechanism of the initial stages of zinc electrowinning was studied using scanning electron microscopy (SEM) and cyclic voltammetry. It is shown that nickel ions are deposited simultaneously onto the zinc crystals which are being formed and onto the still exposed aluminium cathode. As a result of the catalytic activation of the hydrogen ion discharge during the initial stages of the process, conditions are created for the formation of hydrogen bubbles on the uncovered aluminium cathode.

1. Introduction

During the electrowinning stage of hydrometallurgical zinc production, the basic problem related to the quality of the deposited metal and the energy costs of the process is the deleterious effect of small amounts of more electropositive metals, for example: Ni, Co, Cu, Sn, As, Ge, Sb, Fe, etc. [1–9]. Of special practical and theoretical interest in this respect is the specific effect of nickel ions which, in the general case, can be determined as decreasing the zinc current yield typically by 5–10%, due to the depolarization of the hydrogen reaction [8, 10, 11]. It has also been established that in the presence of 5–10 mg l^{-1} nickel ions, the structure and texture of zinc deposits is retained and only the mean size of the crystals decreases [5, 7, 8, 12]. Another characteristic feature of the deleterious effect of the iron group metal impurities is the appearance of the so-called 'induction period' in the electrowinning process, followed by a spontaneous self-dissolution of the previously formed deposit after several hours [5, 11, 13]. It has been established that the duration of this period strongly depends on the current density, temperature and acidity of the electrolyte, as well as the concentration of the metal impurities [4, 10, 13, 15].

From the comprehensive theoretical and practical investigations carried out up to now it may be concluded that the basis of the models seeking to explain the deleterious effect of nickel ions is 'local galvanic cells', where the unevenly deposited Ni behaves as a cathode for hydrogen depolarization with respect to the anodic zinc regions [1, 3, 7, 10, 12].

In spite of the broad acceptance of this concept in the literature and industry, as well as the fairly good explanation of the pitting defects in zinc which it offers, it contains several shortcomings:

a) The exceptionally low concentration of nickel included in the zinc deposit, which is by several orders of magnitude less than its bulk concentration in the solution [12], in terms of the quantity expected by a diffusion-controlled inclusion process.

b) The presence of kinetic limitations for the deposition rate of nickel ions upon zinc substrates, which reaches several μA cm^{-2} [5].

c) The occurrence of an anodic self-dissolution process of the zinc deposit represents a corrosion phenomenon with hydrogen depolarization. This process starts under the conditions of considerable cathodic protection at $I = 5$ A dm^{-2}, and $\eta \sim 200$ mV, thus thermodynamically excluding the possibility for an anodic process.

In addition, it may be noted that studies carried out hitherto neglect the effects exerted by the structural and chemical composition of the electrode substrate. While it may be presumed quite reasonably that the properties and defects in the initial Zn-layers determine the structure of the entire deposit, including the structural malformations and pitting defects [16].

With some exceptions [17], data on the effect of metal inclusions in Al such as Fe, Cu, Zn, etc., always present in the industrially used aluminium cathodes, are absent in the literature. This situation, presents a problem with the mechanism of the zinc electrowinning process during the initial stages, when structural defects and regions with various compositions and properties appear and grow as time elapses [15, 18].

In addition, keeping in mind that nickel is considerably more electropositive than zinc, it may be expected that its specific influence will be expressed most clearly during the early stages, when Ni will be predominantly

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deposited. In this respect, the aim of the present paper
is to study the mechanism and kinetics of the electro-
chemical discharge of zinc ions in the presence of
nickel ions during the initial stages of the process. The
first part of this investigation presents the results and
discusses experiments carried out with a spectrally
pure (Johnson Matthey) aluminium electrode, while
the second part treats data obtained with an alu-
minium electrode containing iron impurities (Riedel).

2. Experimental

The experiments were carried out in a thermostated
three electrode cell in an argon atmosphere. The work-
ing electrode was an aluminium rod 5 mm in diameter,
of surface area $0.2\,cm^2$ (Johnson Matthey) fixed with
respect to a platinum spiral of area $100\,cm^2$ and a
saturated Hg_2SO_4 reference electrode.

The working electrolytes had the following com-
positions: H_2SO_4 $130\,g\,l^{-1}$, $MnSO_4 \cdot H_2O$ $15.4\,g\,l^{-1}$,
$ZnSO_4$ 0.001, 0.01, 1.0 M and Ni^{2+} 10, 30, 60,
$90\,mg\,l^{-1}$. All reagents were MERCK analytical grade
and the solutions were prepared with twice distilled
water. The experiments were carried out at $T = 37°\,C$
and pH = 0.2, 0.5 and 1.0 by adding Na_2CO_3.

The basic electrochemical measurements used cyclic
voltammetry techniques at a scanning rate of 50–
$6000\,mV\,min^{-1}$.

The composition and assay of the Al cathodes and
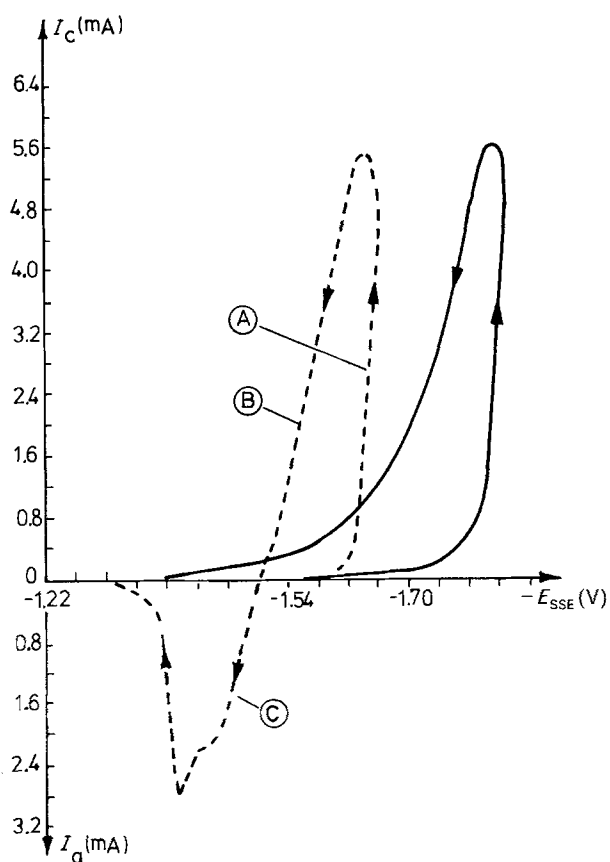the zinc deposited upon them were studied by SEM
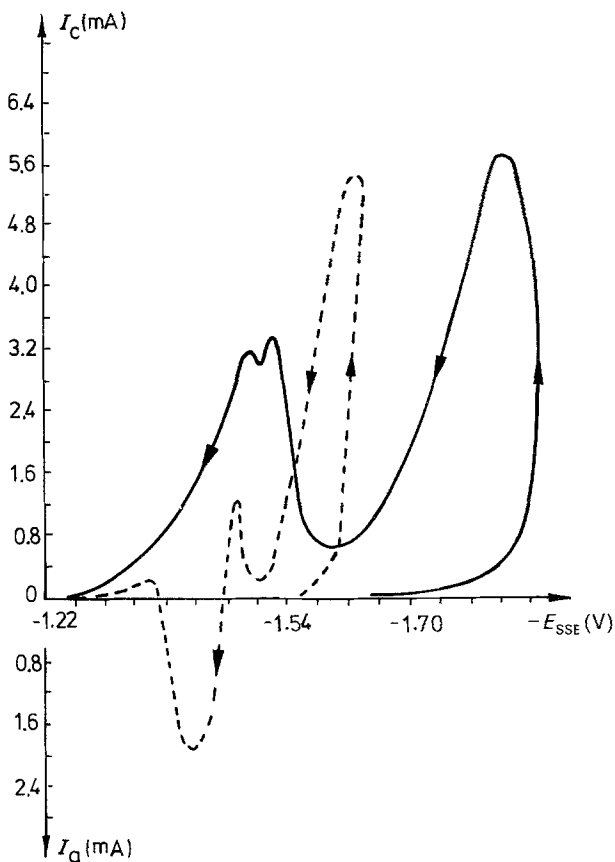

Fig. 2. Cyclic voltammograms obtained in the working electrolyte
with $10\,mg\,l^{-1}$ Ni^{2+} containing $ZnSO_4$: 0.01 M (——); 0.5 M (– – –).
Sweep rate – $50\,mV\,min^{-1}$; pH = 0.2.

methods and electron-microprobe analysis of the
elemental composition with a JEOL Superprobe 773
unit.

3. Experimental results

The cyclic voltammograms in electrolytes with dif-
ferent $ZnSO_4$ concentrations and in the presence of
$10\,mg\,l^{-1}$ nickel ions are shown in Figs 1 and 2. It can
be clearly seen that in both cases well defined potential
regions of zinc deposition and dissolution exist, which
is due to the electrochemical irreversibility of the zinc
deposition–dissolution reaction (low exchange cur-
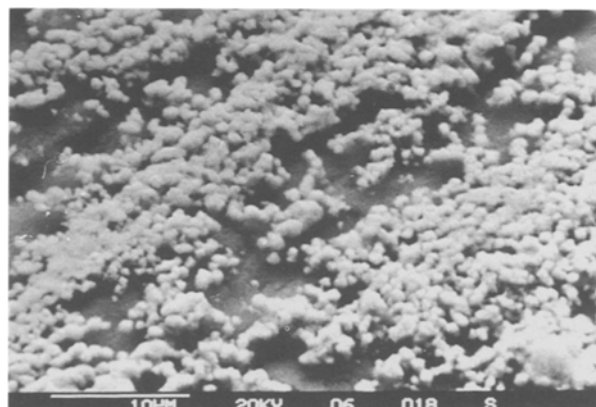rent). In both cases a current hysteresis is observed in

Fig. 1. Cyclic voltammograms obtained in the working electrolyte
containing $ZnSO_4$: 0.01 M (——); 0.5 M (– – –). Sweep rate –
$50\,mV\,min^{-1}$; pH = 0.2.

Fig. 3. Zinc deposit obtained from a working electrolyte containing
$10\,mg\,l^{-1}$ Ni^{2+} and 1 M $ZnSO_4$ at $50\,mA\,cm^{-2}$ – current density.
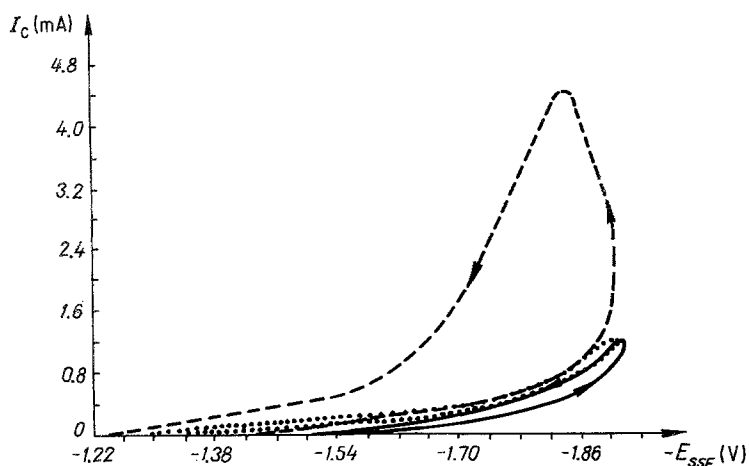$T = 37°\,C$; pH = 0.2, deposition time, $t = 35\,s$.

Fig. 4. Cyclic voltammograms obtained in the supporting (zinc-free) electrolyte containing Ni^{2+}: $10.0\,mg\,l^{-1}$ (——); $30\,mg\,l^{-1}$ (· · ·) and $90\,mg\,l^{-1}$ (— — —). Sweep rate — $50\,mV\,min^{-1}$; pH $= 0.2$.

the cathodic region at potentials more negative than $-1.5\,V_{SSE}$ which is a characteristic feature [19] of a geometrical growth process of 3-D zinc nuclei. A similar shape of the $(I-E)$ curves have been obtained by Despić during the deposition of zinc onto a glassy carbon substrate [20]. The results from the SEM studies at different deposition durations (Fig. 3) confirm the above mentioned, showing a non-uniform zinc deposit with a clearly visible islet structure.

However, several substantial differences exist in the voltamperometric characteristics obtained in the presence and absence of Ni^{2+}.

a) The difference in the quantity of electrical charge for the cathodic and anodic stages for a given zinc concentration is much more pronounced in the presence of nickel ions (essentially in the less concentrated Zn^{2+} electrolytes).

b) In the presence of nickel ions, the anodic part of the scan at $E > -1.5\,V_{SSE}$ (Fig. 2) displays one or two clear-cut current maxima with heights strongly depending on the concentration of zinc and nickel ions.

Taking into consideration that nickel is much more positive than zinc, it may be expected that its effect can be studied regardless of the deposition and dissolution

of zinc. Therefore $(I-E)$ curves were obtained for different nickel ion concentrations in zinc-free supporting electrolyte, (Fig. 4). It is obvious that regardless of its low bulk concentration, nickel considerably changes the strength of the cathodic current, and current hysteresis also exists in this case. One could argue that the current measured under these conditions cannot be the result only of a Faradaic nickel deposition process, due to its extremely low concentration in the bulk, and the measured value is probably a resultant current for the catalysed discharge of hydrogen ions on the deposited nickel.

These initial results provide evidence that the codeposition of nickel ions together with zinc considerably changes the conditions for the initial stages of zinc deposition. It may be claimed that nickel is the metal deposited first because its deposition starts at more positive potentials (Fig. 4). Since its effect may be two-fold, on the one hand upon the mechanism of zinc deposition and dissolution process as a result of alloying and on the other upon the hydrogen evolution process, the Tafel slopes of the different regions of the $(I-E)$ relationships (A–B–C), (Fig. 1), were determined. In addition, similar investigations were carried out at different pH values, (Fig. 5).
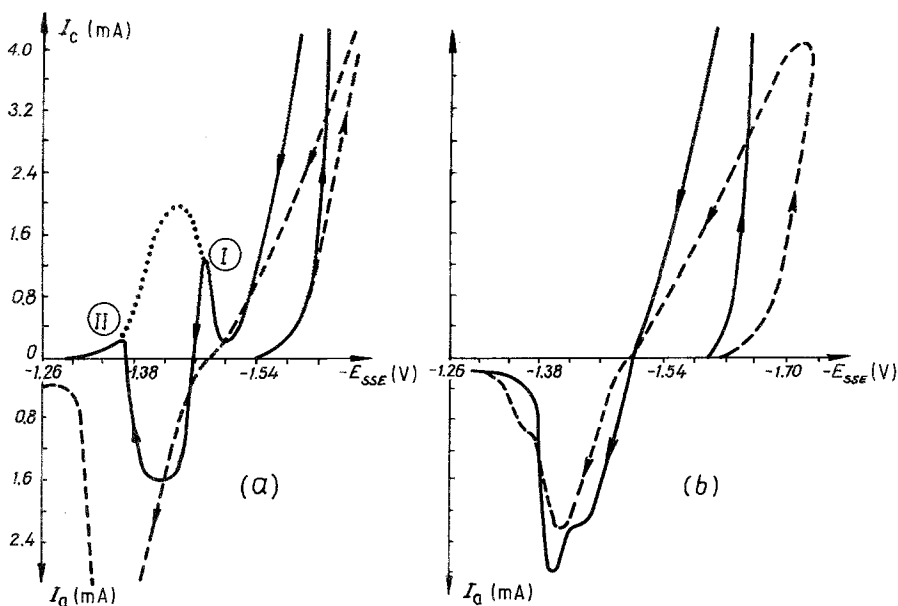

Fig. 5. Cyclic voltammograms obtained in the working electrolyte containing: $ZnSO_4$–$0.5\,M$ with $10\,mg\,l^{-1}$ Ni^{2+} (a), and without Ni^{2+} (b). Sweep rate — $50\,mV$ min^{-1} (——) pH $= 0.2$; (— — —) pH $= 1.0$.
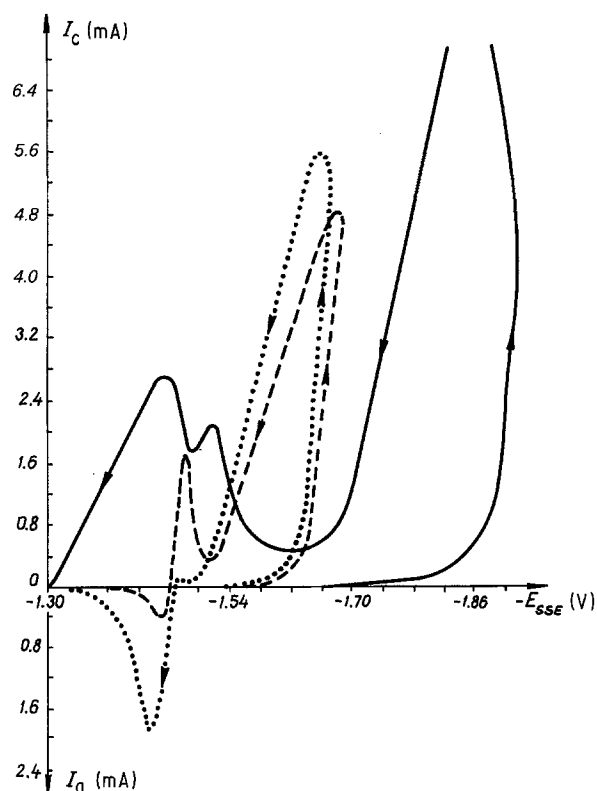
Fig. 6. Cyclic voltammograms obtained in the working electrolyte containing 30 mg l⁻¹ Ni²⁺ and ZnSO₄: 0.01 M (——); 0.5 M (— — —); 1.0 M (· · ·). Sweep rate — 50 mV min⁻¹; pH = 0.2.

The considerable difference in the (b_{cat}) values of the A–B–C regions is quite impressive. While in the first case the polarization curve A is determined totally by the hydrogen ion discharge upon Zn nuclei and the Tafel slope of about 110 mV is typical for this reaction on Zn, in the reverse region (B–C) the Tafel slope of about 30 mV is typical for a two-electron discharge–ionization stage. This is confirmed by the fact that the polarization curve obtained upon a zinc substrate, in the same electrolyte, completely coincides with that traced in the B–C region, (Fig. 1).

But the differences in the (I-E) relationship obtained at various pH values are substantial, (Fig. 5). Obviously, the reaction of H_3O^+ discharge exerts a predominant influence upon the current–voltage relationship, since literture data show [21] that the zinc deposition mechanism is not altered within the pH range 0 to 2. Therefore it may be concluded that the deleterious effect of nickel ions can be studied indirectly by changing the rate of the hydrogen reaction at different nickel ion concentrations. Figure 6 shows the results obtained in an electrolyte containing 30 mg l⁻¹ nickel ions. The comparison of these curves with those presented in Fig. 2, obtained at 10 mg l⁻¹ nickel ions and the same zinc concentration, provides evidence that the strongest effect is observed in the anodic scan region around $E = -1.50$ V, i.e. in the potential range where the zinc deposition current is practically zero. This is easily explained if we accept that during zinc deposition, the codepositing nickel is continuously alloyed and screens the zinc, while at potentials more anodic than -1.5 V$_{SSE}$ regions uncovered by nickel deposited both upon zinc and the still free aluminium cathode remain 'open' to the electrolyte (Fig. 3).

The application of the cyclic voltammetric techniques offers a possibility for convenient investigation of the peculiarities of the electrochemical processes, when different scanning rates are used. In the theory of this method the cases and criteria for reversibility and irreversibility of the electrochemical processes are clearly developed [22].

Since both the electrochemical discharge–ionization of zinc and nickel are typical cases of irreversible processes ($i_0^{Zn} \simeq 10^{-5}$ A cm⁻²; $i_0^{Ni} \simeq 10^{-8}$ A cm⁻²) [23, 24], so the (I-E) relationships obtained at different scanning rates (W) should be strongly affected by (W).

Figs 7a and 7b show the results obtained in a Ni²⁺-free electrolyte as well as in electrolytes containing 60 mg l⁻¹ Ni²⁺ at scanning rates: $W = 60, 600, 3000$ and 6000 mV min⁻¹.
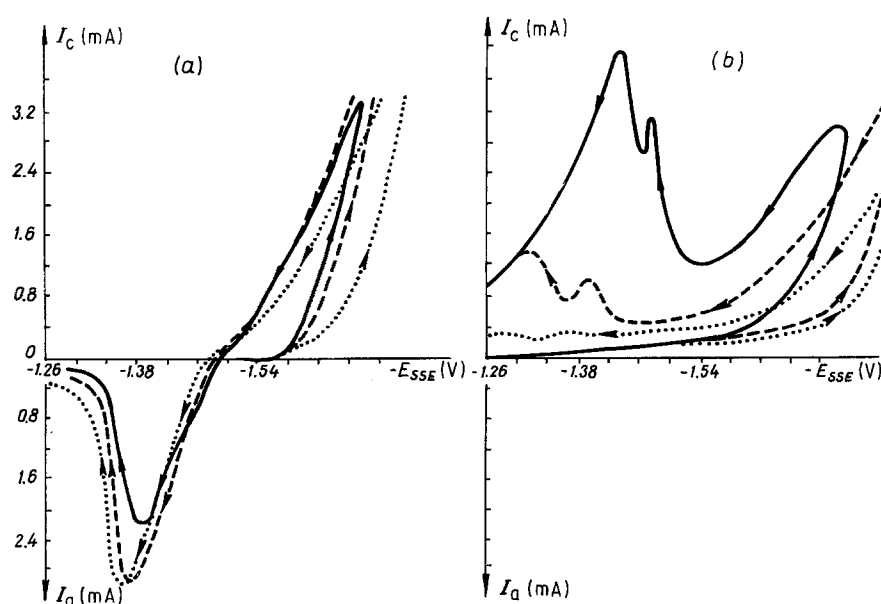

Fig. 7. Cyclic voltammograms obtained at different sweep rates in the working electrolyte (pH = 0.2) containing: a) 0.5 M ZnSO₄ (——) 60 mV min⁻¹; (— — —) 600 mV min⁻¹; (· · ·) 3000 mV min⁻¹. b) 0.5 M ZnSO₄ with 60 mg l⁻¹ Ni²⁺. (——) 600 mV min⁻¹; (— — —) 3000 mV min⁻¹; (· · ·) 6000 mV min⁻¹.

4. Discussion

As already mentioned in the introduction, the basic problem related to the deleterious effect of Ni^{2+} is not only a practical, but also a theoretical, major issue, linked with the mechanism of pitting defect formation and development. In addition it was suggested that the local 'galvanic cell' model fails to provide a good explanation of the nature of and the factors determining the existence of an 'induction period', following which the electrochemical parameters of the system are radically altered [25].

Figs 1 and 2 provide unambiguous evidence that the character of zinc nucleation is not changed in the presence of nickel but, owing to the codeposition of the latter together with zinc, as upon the uncovered aluminium cathode, the overall current of the system is higher at constant potential owing to the catalytically activated hydrogen reaction by deposited nickel.

A very interesting phenomenon observed in Figs 2, 5 and 6 is the abrupt increase of the cathodic current at potentials when the zinc deposition current is near to zero ($E \approx 1.50 V_{SSE}$). The peculiarity in this case is that the overall cathode current maximum shown with a dashed line in Fig. 5a, which is due to the Ni-catalysed hydrogen reaction, splits into two parts (I and II) with the zinc equilibrium potential between them. In our opinion, the interpretation of these current maxima can be related solely with the presence of two types of nickel deposit: Ni upon the zinc crystallites, revealed as (i_{peak}-I) and nickel upon the aluminium cathode (i_{peak}-II).

A very important point is that the increase of the current at maximum (II) occurs after an anodic dissolution process of the deposited zinc and it appears only after complete dissolution of the zinc deposit. So, as is shown in Fig.8, when the quality of the deposited zinc is sufficient (after deposition time 15 min at $E = -1.65 V_{SSE}$) the cathodic current maximum (II) does not appear, owing to the strong anodic process of zinc dissolution at the same potential region.

It was also noted that both maxima increase proportionally with the concentration of Ni^{2+} (Figs 2 and 6). It follows that early in the initial stages active regions for the evolution of hydrogen bubbles are formed on the aluminium cathode which, owing to the current screening effect [26], retain pitting defects along the entire zinc deposit, regardless of the deposition time. Thus an explanation is provided for the fact that, in the presence of Ni^{2+}, zinc deposited during the 'induction period', i.e. prior to the active self-dissolution, also has pitting defects.

5. Conclusion

The cyclic voltammetric and electron-microscopic investigations of the mechanism of the effect exerted by Ni^{2+} during the deposition of zinc from sulphate electrolytes lead to the conclusion that nickel ions are deposited simultaneously on the zinc crystals which are being formed as well as onto the bare regions of
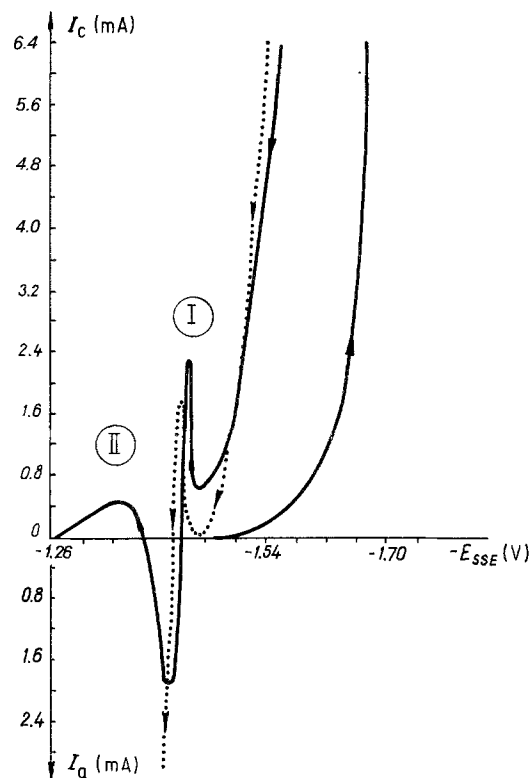

Fig. 8. Cyclic voltammograms obtained in the working electrolyte containing 0.5 M $ZnSO_4$ and 10 mg l^{-1} Ni^{2+}. Sweep rate — 60 mV min^{-1}; pH = 0.2. (——) immediately scanning back after reaching $E = -1.65 V_{SSE}$; ($\cdots$) after deposition time 15 min at $E = -1.65 V_{SSE}$.

the aluminium cathode. As a result of the catalytic activation of hydrogen ion discharge by the locally distributed nickel upon the aluminium substrate, during the initial stages of the process, conditions are created for the initiation and development of a gaseous phase (hydrogen bubbles) which creates a local redistribution of the current and, as a result, structural defects in the form of pits.

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