Electrochemical activation of the electroless deposition of Ni–P alloy and phase structure characterization of the deposit
Part II: Single bath system

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Abstract

The process of electroless Ni plating (EP) was activated by the cathodic deposition of precursors of Ni in the same bath in which EP takes place. The current density (c.d.), duration of cathodic activation, as well as the duration of subsequent EP were varied and the effect of these parameters on the phase composition of the resulting Ni–P deposits was determined by anodic linear sweep voltammetry (ALSV). It was found that electrochemical activation can be achieved with relatively low c.d. and short current pulses, to run at rates comparable to EP activated in other ways. The rate of EP alone was found to be in the range between 1 and 5 mC cm^{-2} s^{-1}, regardless of the activation c.d. or the amount of electrochemically deposited Ni precursors. A synergistic effect was obtained in cases when a little low c.d. cathodic current was passed simultaneously with the EP. The alloys were found to consist of a solid solution of P in Ni, as well as of some phosphide compounds and pure Ni (at increasing activation c.d.). During EP, however, only the solid solution was deposited. The phase structure of the deposit can be varied to a certain extent by the activation c.d.

1. Introduction

In a previous communication (Part I) [1] the possibility of the electrochemical activation of electroless plating (EP) was reported. Following the usual practice of EP on 'noncatalytic' surfaces [2], the activation was carried out in a separate bath prior to immersion of the samples in a conventional EP bath containing hypophosphite as the reducing agent for nickel deposition. It was shown that this could be successfully achieved with good control of the activation process parameters and, in particular, the c.d. and quantity of electricity used for forming the precursors necessary to start active metal deposition. Using the method of anodic linear sweep voltammetry for phase structure determination [3], it was shown that the EP deposit obtained in this way has the same characteristics as the nickel phosphorous alloy obtained after conventional activation of the EP deposition.

The dual bath process has the disadvantage of relative complexity, requiring treatment of the samples in three steps: dipping in the activation bath, rinsing in between the two baths and dipping into the EP bath. Hence, performing both activation and EP in a single bath would have a distinct advantage. Attempts at such a single bath process can be found in the literature, whereby activation was performed by what is essentially the electrochemical process of dipping the samples to be plated into the EP bath and touching them with some 'electronegative metal' or 'connecting them to a battery' [4]. It appears that no systematic investigation of such an activation process defining the process parameters and their effect on the resulting EP has been carried out.

In the present investigation activation was performed by cathodic deposition of precursors of the same metal as that to be plated in the same bath in which the EP subsequently takes place. The process parameters varied were the c.d. of the activation, j_{act}, and the duration of cathodic current pulses, t_{act}, imposed upon samples, as well as the duration of subsequent EP, t_{EP}. Moreover, the effect of these parameters on the phase composition of the resulting deposits was determined.

2. Experimental details

The experiments were performed in a bath composed of an aqueous solution of 0.1 M NiSO$_4$, 0.5 M NH$_4$Cl and 0.5 M NaH$_2$PO$_2$ at a pH of 8.7 at 40 °C.

Electrochemical Ni deposition followed by EP was carried out on a glassy carbon rotating disc of 0.07 cm^2

surface area rotating at a speed of 1000 rpm. The substrate was prepared by polishing with 0.05 μm Buchler alumina and cleaning in an ultrasonic bath in 18 mΩ water before each run.

The entire process was carried out in a glass cell with provisions for electrochemical activation; that is, for making the rotating substrate a cathode facing a Pt counter electrode as the anode, and a reference electrode (saturated calomel electrode) for measuring the cathode potential.

Current pulses of the desired duration were provided by a galvanostat/potentiostat (PAR 273). After the activation and EP, the electrode was transferred to another cell containing 1 M NaCl – 0.1 M HCl solution and subjected to ALSV, performed by a universal programmer (PAR 173) connected to the cell via a potentiostat (PAR 175) and recorded on an XYt recorder at a sweep rate of 5 mV s^{-1}. ALSV was carried out at room temperature.

All the solutions were made of reagent grade chemicals and Millipore (18 MΩ) water.

3. Results and discussion

The galvanostatic transients recorded upon imposing different constant current pulses are shown in Figure 1. Overshoots amounting to 270 mV at the highest current density applied (100 mA cm^{-2}) were similar to those obtained in solutions not containing hypophosphite (Part I [1]), except for a somewhat shorter duration before steady state potentials were reached. Hence, the presence of hypophosphite was found not to affect the electrochemical process. Some 50 to 100 ms were sufficient for the steady state to be achieved.

The results of ALSV, presented in Figure 2, were obtained when the samples were taken out of solution immediately after cathodic activation to a constant cathodic charge of 270 mC cm^{-2} was stopped; that is,
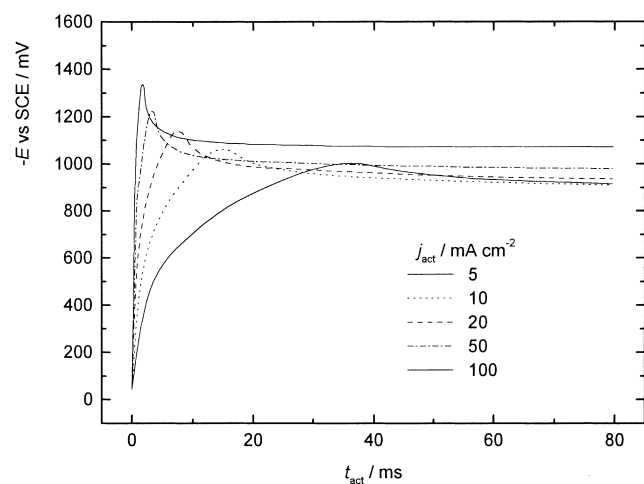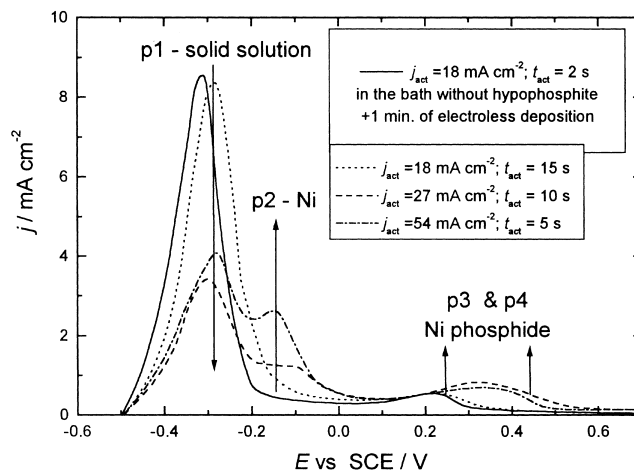
Fig. 2. ALSV record of deposits obtained during activation with different c.d. and a constant amount of deposited metal (equivalent to 270 mC cm^{-2}) in a single bath, compared to the ALSV (solid line) obtained upon activation with 36 mC cm^{-2} in a separate bath and 1 min of EP.

they stayed in solution an ever shorter time the higher the activation c.d. The voltammograms are seen to exhibit up to four peaks, denoted by p_1, p_2, p_3 and p_4.

The voltammograms were obtained after activation was conducted in the same bath in which EP was to take place. The exception is the ALSV represented by the solid line which was obtained when the activation was carried out in a separate bath prior to immersion of the samples in the EP bath (cf. Part I of this communication [1]). In the case of the lowest activation c.d., when contact with the solution lasted for 15 s, the ALSV showed the same effect as that obtained by the dual bath process, except for a small shift in the peak potential and a faint kink at about −200 mV. However, it should be noted that more intensive EP took place in this case, as the amount of electricity obtained under the peaks upon anodic dissolution corresponded to that obtained after 60 s of EP when the activation was done in a separate bath.

With decreasing contact time with the solution (i.e., increasing activation c.d.), the first part of the voltammograms splits into two peaks (at −300 and −150 mV vs SCE). This is not unexpected in view of the fact that upon increasing the current density the residence time of the samples in the bath and, hence, the duration of the simultaneously running EP process decreases, i.e. the fraction of chemically deposited alloy must also decrease. That was indeed found, as seen in Figure 2, in the decrease of the charge under peak p_1, ascribed to the solid solution of P in Ni, and the increase in the fraction of charge corresponding to peak p_2 upon increasing c.d. On the basis of previous experiments [1], peak p_2 reflects the dissolution of pure Ni.

All the voltammograms contained peaks p_3 and p_4, that part of the deposit dissolving at relatively positive potentials, between 200 and 550 mV vs SCE. (On repeating the anodic sweep, only the baseline was

Fig. 1. Galvanostatic transients upon application of different activation c.d.

recorded, implying that all the deposit was dissolved.) The charge of peak p3, which was ascribed to Ni phosphide, increases. This may be explained by recalling the findings of other authors [5, 6] which state that electrochemically obtained binary Ni–P alloys may contain up to 18% of P. In contrast to this, electroless Ni–P alloys, when plated from alkaline baths, can contain up to 7% of P [7]. Keeping in mind that upon increasing the current density an ever larger fraction of P is deposited in the electrochemical process, it can be concluded from Figure 2 that the formation of the Ni_2P compound is increasingly favored with increasing of the c.d.

In the next series of runs, the effects of both the c.d. and the duration of activation, as well as of the total time allowed for EP, were investigated.

At the rather low activation c.d. of 10 mA cm^{-2} the anodic dissolution voltammogram, seen in Figure 3(a), consists of a single peak at −0.3 V and a long tail extending to +0.4 V. The quantities of the deposit, in terms of the equivalent quantity of electricity obtained by integration of the voltammograms, are plotted in Figure 4(a). It can be seen that the amount of electricity obtained from complete anodic dissolution, Q_{tot}, (i.e. the amount of the deposit) as well as that under the first

Fig. 4. Dependence of the total amount of electricity, Q_{tot}, as well as of those under different peaks, Q_{pi}, obtained by integration of the ALSVs of Figure 3(a) and (b). Q_{act} is the amount of electricity consumed in the process of activation.

peak, Q_{p1}, increase in some proportion with time (about 21 and 19 mC cm^{-2} s^{-1}, resp.).

However, assuming 100% efficiency at that j_{act}, some 10 mC cm^{-2} s^{-1} are deposited electrochemically. Hence, only those quantities in excess of that indicated by the solid line should reflect the effect of EP.

The plot of Figure 4(a) indicates that EP does not start immediately. Steady EP only occurs after the first 10 s at a rate of 11 mC cm^{-2} s^{-1}.

When the activation was stopped after 5 s and the sample left in the bath for EP to continue, the anodic dissolution voltammograms (Figure 5(a)) exhibit the same shape as those in Figure 3(a), but with a significantly lower increase in the amount of the deposit with time. Thus, the plot in Figure 6(a) (where the amounts of electricity under the peaks are given as a function of the total time $t_{tot} = t_{act} + t_{EP}$) shows that the rate of EP amounts to only about 4 mC cm^{-2} s^{-1}.

Similar experiments were performed with an activation c.d. of 20 mA cm^{-2}. Keeping the pulse durations similar to those at 10 mA cm^{-2}, significantly larger Q_{act} (up to 600 mC cm^{-2}) were passed. As can be seen in Figure 3(b), at low values of Q_{act} (up to 100 mC cm^{-2}) the ALSVs are similar to those obtained at an activation
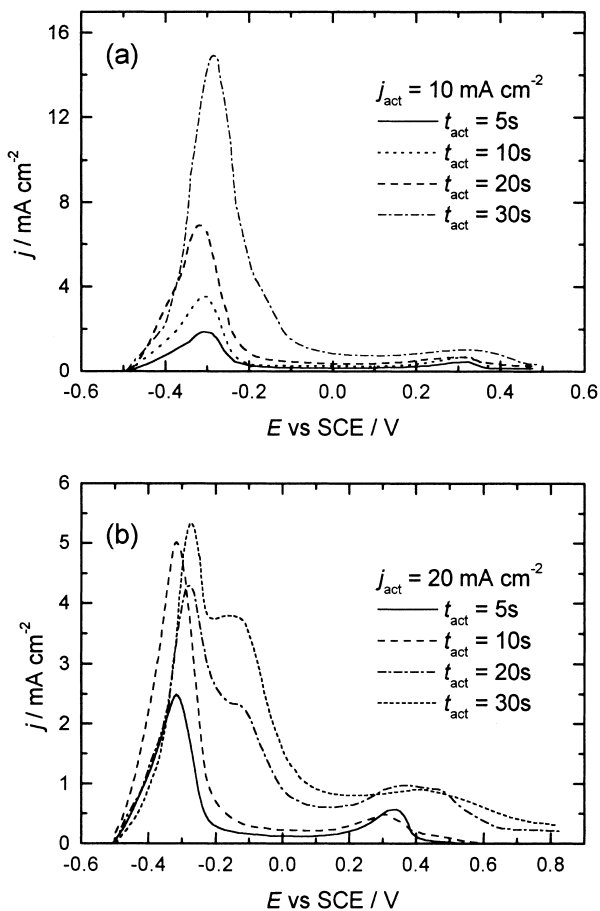

Fig. 3. ALSV of deposits obtained during simultaneous activation and EP at two different activation c.d. and for different durations of deposition.
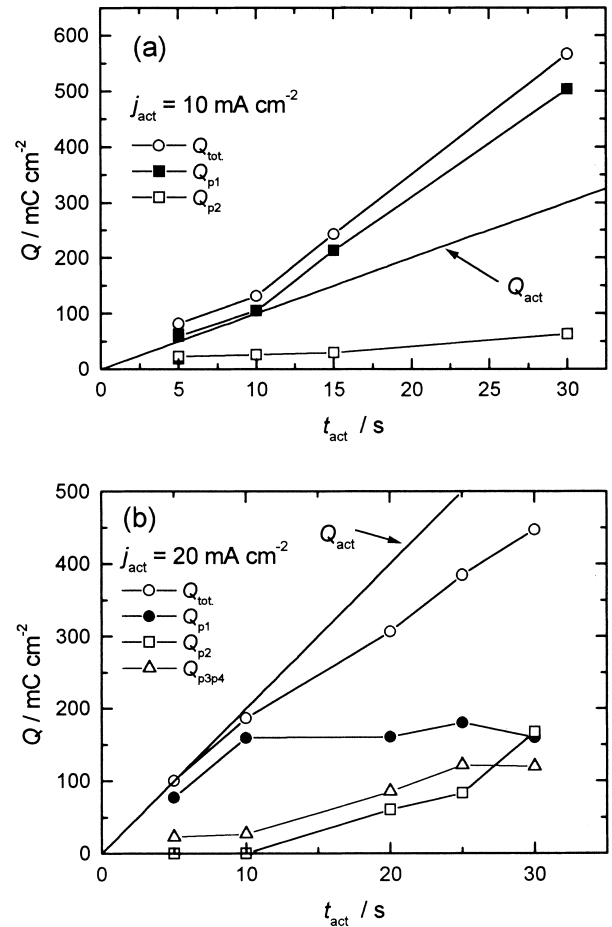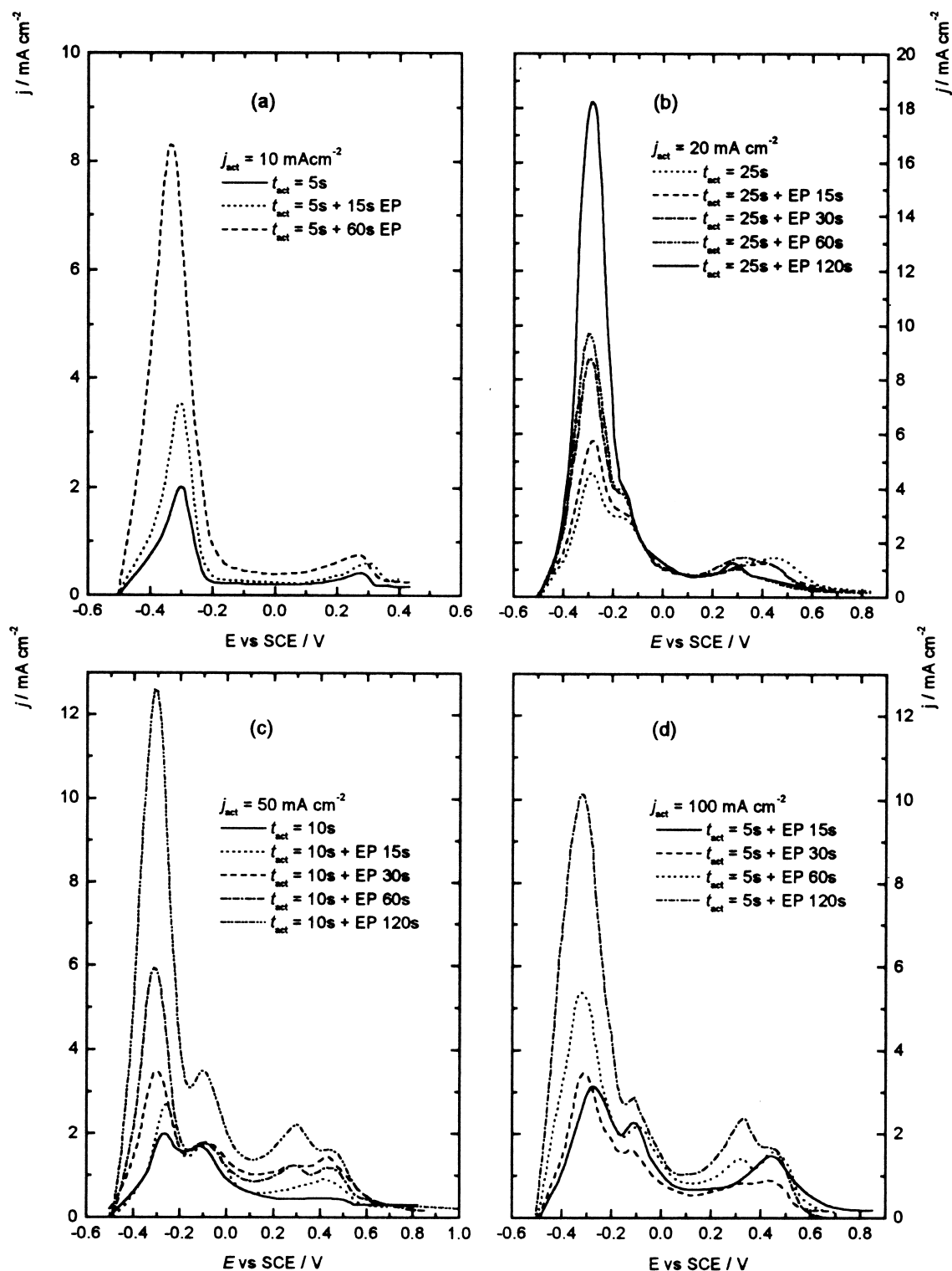
Fig. 5. ALSV of deposits obtained after a constant amount of electricity had been consumed on the activation and different durations of EP. (a) 10 mA cm^{-2}, 50 mC cm^{-2}; (b) 20 mA cm^{-2}, 500 mC cm^{-2}, (c) 50 mA cm^{-2}, 500 mC cm^{-2}, (d) 100 mA cm^{-2}, 500 mC cm^{-2}.

c.d. of 10 mA cm^{-2}, except for the development of peak p_3 at $+0.3$ V.

However, upon prolonged activation, peak p_2 starts to develop at about -0.1 V, as well as peak p_4 which appears around $+0.45$ V.

Deconvolution of the peaks was carried out using the asymmetric double sigmoidal multipeak fitting method.

The growth of the total amount of electricity under the ALSV, as well as those under each peak, are given in Figure 4(b). It may be seen that the rate (slope) of deposition by both the electrochemical discharge and the EP running simultaneously amounts to 14 mC cm^{-2}. This is less than that calculated from the activation c.d. alone (20 mC cm^{-2} s^{-1}), implying a significant decrease
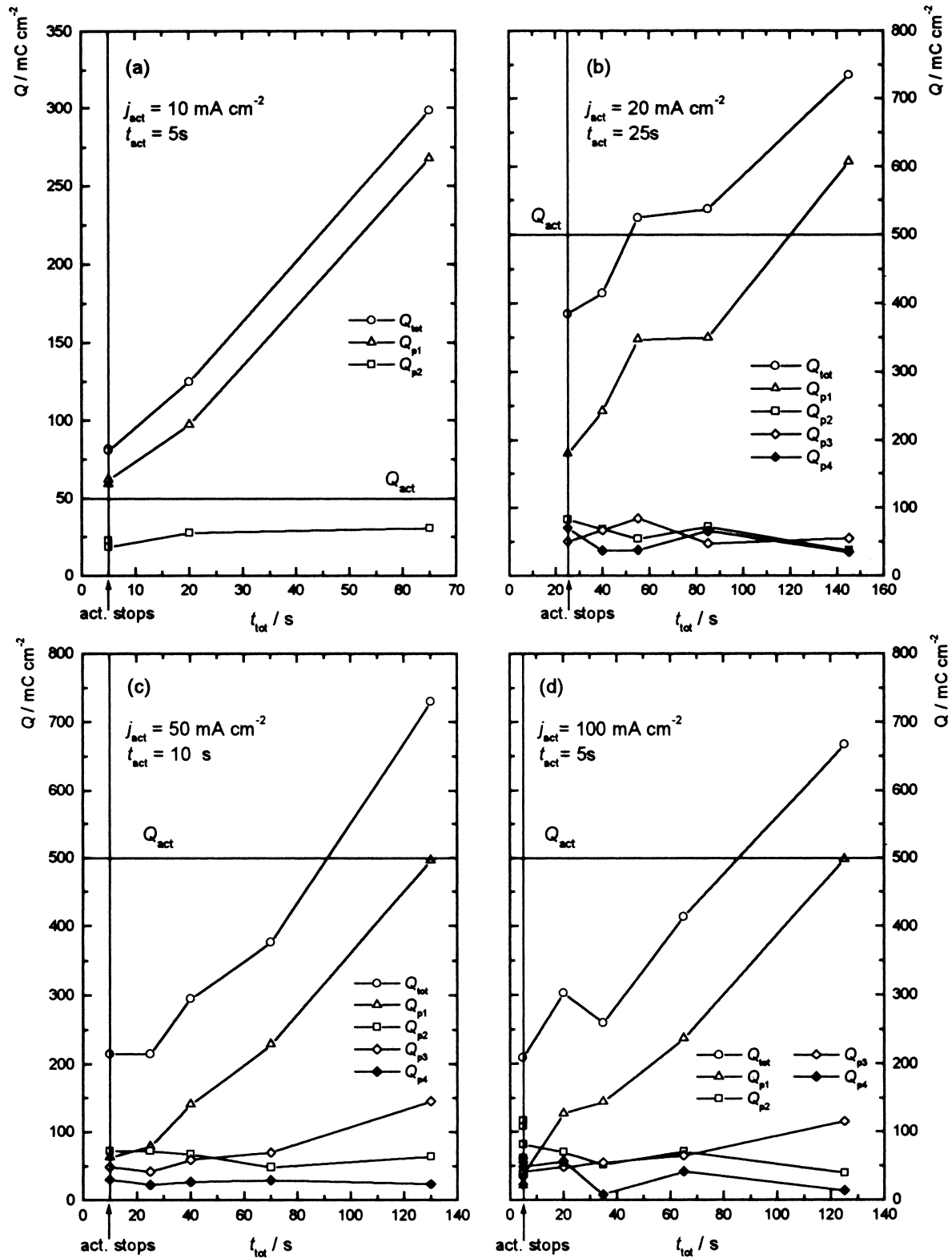
Fig. 6. Dependence of the total amount of electricity, Q_{tot}, as well as of those under different peaks, Q_{pi}, obtained by the integration of ALSVs of Figure 5(a)–(d), on the total time of immersion of the samples in the bath.

in the current efficiency of the activation. At the longest time of activation (30 s), a non homogeneous and loose deposit was obtained, which exhibited a tendency to peel off. This is the reason for the deviation of the last point in Figure 4(b).

Peak p_1 was found to grow for the first 10 s only, but further activation did not produce further growth. Peak p_3 exhibited some growth at the beginning. The main growth after the first 10 s of activation was that of peak p_2, meaning that deposition of Ni is favoured. However,

when activation with 20 mA cm^{-2} was stopped after 25 s (500 mC cm^{-2}) and EP allowed to continue for different time periods after the activation (Figure 5(b)), only peak p$_1$ continued to grow, all other peaks remaining virtually at their initial Q values, varying erratically within rather large limits of error (Figure 6(b)). Within the first 25 s only 380 mC cm^{-2} were deposited by both electrochemical deposition and EP, although 500 mC cm^{-2} of electricity were spent on the former, implying a current efficiency of less than 76%. The rate of the subsequent EP was found to be only about 2.9 mC cm^{-2} s^{-1}.

In the next series of runs the activation was carried out with 50 mA cm^{-2} for 10 s (500 mC cm^{-2}) and then EP was allowed to take place for different periods. The results are presented in Figure 5(c) from which it may be seen that four peaks developed after prolonged EP (120 s). Deconvolution of the peaks was carried out using the procedure cited above. With prolonged deposition time peak p$_1$ is seen to grow in proportion to deposition time (Figure 6(c)) so that an equivalent of about 4 mC cm^{-2} s^{-1} of the metal are deposited. Hence, this leaves no doubt that a solid solution of P in Ni was the main result of EP after the activation ended. Peak p$_2$ remains virtually constant within rather large error limits (varying erratically between 50 and 80 mC cm^{-2}) implying that the phase, the existence of which it reflects, is formed only during the electrochemical process. Peak p$_3$ exhibits some growth, while peak p$_4$ again remains virtually constant.

The total amount of the deposit, represented by the equivalent amount of electricity obtained, increases proportionally to the time of EP, the rate of growth being about 4.8 mC cm^{-2} s^{-1}. Within the first 10 s, when electrodeposition and EP ran simultaneously, the amount of electricity obtained by dissolution was about 214 mC cm^{-2}. Considering that within that time about 48 mC cm^{-2} were obtained by EP, the electrochemical

activation appears to have given only 166 mC cm^{-2} of the deposit. Compared to the 500 mC cm^{-2} of electricity used for activation, it gives a rather low current efficiency of Ni deposition of only 33%, the rest probably being spent on the cathodic reduction of hypophosphite or on hydrogen evolution.

Activation with 100 mA cm^{-2} resulted in rather poor reproducibility of the ALSVs. However, the four peaks are also well pronounced here (Figure 5(d)), peak p$_3$ being significantly larger than in the previous cases, and on some recordings being overwhelming. Also, a knee appeared before peak p$_1$ at some −0.4 V. In the experiment in which the activation was carried out for 5 s (500 mC cm^{-2}) and then EP allowed to take place for different time periods (Figure 6(d)), the rate of growth of the deposit amounts to 3.5 to 4.5 mC cm^{-2} s^{-1}; that is, it may be seen to stay more or less the same as in the previous cases of lower activation c.d. During prolonged EP it can be seen that, as in the previous cases, the first peak grows steadily, while the other peaks stop growing after the end of activation.

An observation common to all activation c.d. is that the rate of growth of the deposit by EP subsides after the activation is ended. Typically, the rate of growth of the deposit during the activation with 10 mA cm^{-2}

Fig. 8. ALSV records of deposits obtained after 10 mC cm^{-2} of electricity consumed at different c.d. and 30 s of subsequent EP. Q'_{act} is the amount of electricity obtained in anodic dissolution after activation alone; Q the amount of electricity after the entire process; and ΔQ the amount of electricity reflecting the amount of metal obtained by EP after the activation had ended.
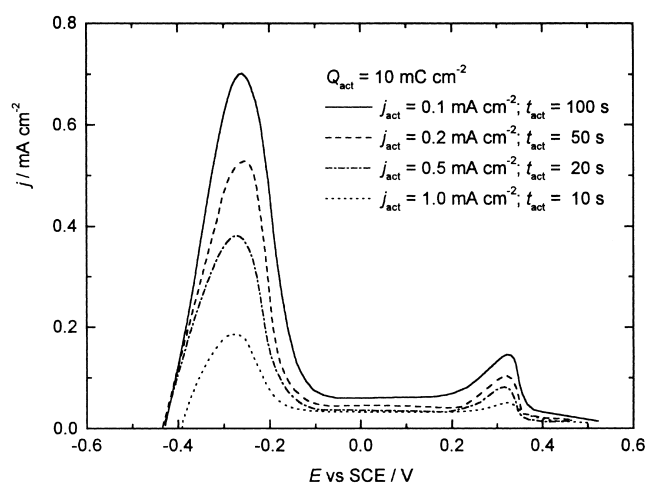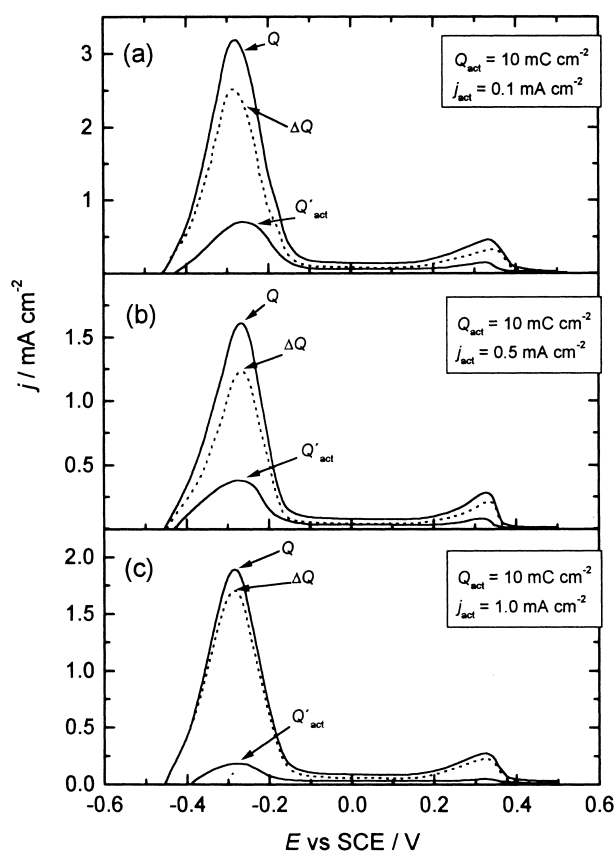

Fig. 7. ALSV records of deposits obtained by activation and simultaneous EP with c.d. between 0.1 and 1 mA cm^{-2} for a total amount of electricity consumed on the activation of 10 mC cm^{-2} and different times of immersion of the samples in the bath.

Table 1. Results of integration of the ALSV presented in Figure 8

j_{act} /mA cm^{-2}	t /s	Q'_{act} /mC cm^{-2}	Q/t /mC cm^{-2} s^{-1}	Q_{tot} /mC cm^{-2}	ΔQ /mC cm^{-2}	$\Delta Q/t$ /mC cm^{-2} s^{-1}
0.1	100	32.8	0.33	124.5	91.7	3.06
0.5	20	17.4	0.87	60.8	43.4	1.45
1.0	10	9.9	0.99	69.5	59.6	2.0

(Figure 4(a)) is 21 mC cm^{-2} s^{-1} of which at least 11 mC cm^{-2} s^{-1} should be deposited by EP, while after the activation is ended (Figure 6(a)), the rate is reduced to 3.8 mC cm^{-2}. The rate of EP remains virtually constant and independent of the c.d. or duration of activation (3–5 mC cm^{-2} s^{-1}) (Figure 6).

The different rate of EP in the two cases (i.e., during electrochemical activation and after its cessation) can be explained in the following terms. After the activation stops and the surface of the substrate is covered with an already substantial amount of the deposit, further deposition is likely to be epitaxial as no new nucleation is likely to take place. In contrast, when EP takes place while some metal is simultaneously deposited electrochemically, it is likely that new nuclei are formed continuously as growth sites during the electrodeposition and thus stimulate EP.

In another series of runs the region of very low activation c.d. and a low quantity of metal precursors, equivalent to 10 mC cm^{-2}, was investigated. It was found that for activation c.d. below 0.1 mA cm^{-2}, even for 100 s, no deposit could be detected by subsequent ALSV. Hence, it can be concluded that an amount of electricity of at least 10 mC cm^{-2} is needed for a sufficient amount of precursors for commencement of EP to be obtained.

For activation c.d. in the range between 0.1 and 1 mA cm^{-2} and with the samples taken out of the bath immediately after the cessation of activation, the voltammograms shown in Figure 7 were obtained. It can be seen that the higher the c.d., but also the shorter the time of immersion in the bath, the lower the yield of the metal. However, when the rate of deposition is calculated as Q/t, it increases with increasing c.d., although the current efficiency obviously falls below 100%.

When the samples were left in the bath after activation for 30 s for EP to take place, significant growth of the deposit was found, as shown in Figure 8 (the ALSV denoted by Q'_{act} being taken from Figure 7). As shown in Table 1, it is interesting to note that the growth was greatest after activation with the lowest c.d., although the 30 s period represents only a 30% increase in duration of EP compared to the 150% and 300% increased duration in the case of the other two activation c.d.'s.

Q'_{act} is larger than Q_{act} (except at $j_{act} = 1$ mA cm^{-2}) and increases with decreasing j_{act}. This may be explained by the fact that EP takes place simultaneously with cathodic deposition and that the process lasts longer the lower the j_{act}.

4. Conclusions

(i) Electrochemical activation can be done efficiently in the same bath in which EP is performed, to run at rates common to EP activated in other ways.

(ii) The rate of EP alone appears not to be sensitive to either the activation c.d. or amount of electrochemically deposited precursors and lies in the range between 1 and 5 mC cm^{-2} s^{-1}.

(iii) Increase in activation c.d. gives an increasing amount of pure Ni in the deposit.

(iv) Investigations at the lower limit of the activation c.d. and quantity of precursors (0.1 to 1 mA cm^{-2} and 10 mC cm^{-2}) reveal that activation can be done under such conditions and that EP gives deposits of the same phase composition as those obtained with an order of magnitude larger amounts of metal deposited electrochemically. Although the rate of deposition during activation was found to be significantly lower, the rate of EP after the activation ended, $\Delta Q/t$, as shown in Table 1, was found to be of the same order as that obtained in previous experiments with much larger c.d.'s and precursor quantities.

(v) If faster deposition is desired than that obtained by EP alone, some cathodic current at low current density should be passed continuously through the system simultaneously with EP. A synergistic effect is expected.

(vi) ALSV proved to be an adequate tool for determining the phase structure and phase composition of the Ni–P alloys.

(vii) Alloys were found to consist mainly of a solid solution of P in Ni. In the early phases of growth, during and after the activation ended, some phosphide compounds, as well as pure Ni (at increasing activation c.d.), were formed. During EP, however, it appears that only the solid solution is deposited.

Apology

The editor apologies for delay to this paper.

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