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Electrochemical activation of the electroless deposition of Ni–P alloy and phase structure characterization of the deposit.
Part I: Dual bath system[#]

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Abstract

A typical low temperature alkaline bath was chosen for the investigation of the effect of electrochemical activation on the efficiency of the electroless deposition of Ni and on the phase structure of the Ni–P alloys obtained. Electrochemical deposition was separated from chemical deposition by employing a two bath sequence, the first (i.e., the bath for electrochemical activation) being free of reducing agent. It was found that an activation current density, as well as an amount of precursors at the surface larger than a critical value (0.5 mA cm^{-2} and 8 mC cm^{-2}, respectively) are required for the electroless process to take place. The phenomenon was explained in terms of nucleation theory. Anodic linear sweep voltammetry (ALSV) of the Ni–P alloys obtained after electrochemical activation, as well as of those obtained after chemical (Sn–Pd) activation, indicated the presence of two dominant phases, that is, a solid solution of P in Ni, and a nickel phosphide compound, most probably Ni_2P. It was also shown that changes in the phase structure of the electroless Ni–P deposit upon thermal treatment may be followed by employing (ALSV).

1. Introduction

In the case of nonconducting surfaces, electroless plating (EP) requires activation as well as sensitization of the surface, to precede the process of the chemical reduction of ions of the depositing metal from the solution and its deposition on the object to be plated [1]. Usually activation is carried out by chemical means, by depositing precursors of a metal different to the one to be deposited (Pd, Ag). This practice requires that activation and EP be carried out in separate baths with some rinsing of the objects to be plated in between. It is well known that the number, as well as the density and size, of nuclei of the activating metal are critical for the initial rate and efficiency of subsequent EP [1].

In this investigation an attempt was made to carry out the activation by electrochemical deposition of the precursors of metal grains of the same metal in order to provide centres of preference for the subsequent massive deposition of the metal. This attempt was based on the experience that an electrochemical process can be more easily manipulated and conducted than a chemical process. In a cathodic activation both the quantity of activating metal and the nucleation density can be well controlled, the former being directly proportional to the quantity of electricity passed, and the latter (the nucleation rate) being dependent on the applied cathodic overpotential. Moreover, while conventional EP requires separate baths, in electrochemical activation both processes can be performed in one and the same place, which makes for a significantly simpler and cheaper operation.

There have been attempts to perform what is essentially an electrochemical activation [2, 3], by contacting a sample to be plated, which is already located in an EP bath, by some 'electronegative' metal for a few seconds

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[#] Reported in part at the 49th ISE Meeting, Paris 1997.

or connecting it to a battery. However, these attempts were entirely empirical, relying on the skill of the plater.

In the present work the deposition of nickel on an electrically conducting surface by EP was investigated with electrochemically performed activation. The conditions of activation were varied either by depositing the activating metal at one and the same quantity of electricity, but at different overpotentials (current densities), or by varying the time of deposition at a fixed overpotential.

Activation and deposition were first carried out in separate baths. The influence of electrochemical activation on the EP process was further investigated in the same bath in which EP was conducted. These results will be reported in Part II of this communication.

2. Experimental details

Two different baths were used, one for activation and another for EP. Activation was first carried out in a solution of a typical formulation used for chemical activation prior to EP [4]: 0.25 g l^{-1} $PdCl_2$ and 2.5 g l^{-1} HCl. The activation was carried out in still electrolyte at 25 °C for 30 s.

In another set of experiments electrochemical activation was performed in a solution containing 0.1 M $NiSO_4$ and 0.5 M NH_4Cl (pH 8.7) at 40 °C. Nickel was electrodeposited on glassy carbon rotating disc electrodes of 0.07 cm^2 at a rotation speed of 1000 rpm. A standard electrochemical cell and instrumental set-up were employed enabling activation to be performed by galvanostatic pulses of fixed current and duration.

EP was performed in a bath of the same composition as that for electrochemical activation but also containing sodium hypophosphite at a concentration of 0.5 M NaH_2PO_2, as a reducing agent. The bath was operated at 40 °C. The process in the EP bath was carried out without stirring. The electrodes were prepared by polishing (0.05 μ Buchler alumina) and cleaning in an ultrasonic bath (18 MΩ water) before each run.

The deposits were analysed for phase structure by anodic linear sweep voltammetry (ALSV) [5]. ALSV was performed in a standard electrochemical cell by a universal programmer (PAR 173) connected to the cell via a potentiostat (PAR 175), which enabled sweeping of the potential of the sample from a certain cathodic to a certain anodic limit and recording the current response on an X–Y–t recorder. The ALSV analyses were performed in 1 M NaCl–0.1 M HCl solutions to overcome passivation of the nickel at a sweep rate of 5 mV s^{-1}. The ALSV experiments were carried out at room temperature.

All the electrolytes were made of reagent grade chemicals and Millipore (18 MΩ) water. Each experiment followed the procedure: polishing → cleaning → activation → rinsing (in the case of chemical activation) → EP → rinsing → ALSV. The solutions were deaerated by purging with purified nitrogen although it was established that deaeration had no effect on the results.

3. Results

The galvanostatic transients recorded during the process of activation are shown in Figure 1. They are characterized by 'overshoots' settling to steady-state potentials after some 100 ms. The overshoots are larger and of shorter duration the higher the current density in the galvanostatic pulse and quantity, up to some 200 mV for the highest current density used (100 mA cm^{-2}). The polarization curve pertaining to Ni deposition in the process of activation is shown in Figure 2. The steady-state potential values were taken after a constant quantity of electricity (1000 mC cm^{-2}) was passed with the activation pulse, implying longer pulse duration the smaller the activation current density. A nonlinear Tafel plot is obtained, with an increase of polarization tending to some 60 mV dec^{-1} in the low current density region.

ALSV recordings in chloride containing solution gave the voltammograms shown in Figure 3 for the deposit obtained after chemical activation and EP lasting for 30 s. One large anodic peak is obtained at a peak potential of about −0.3 V vs SCE and a significantly smaller peak at +0.3 V vs SCE with some anodic current in between.

With electrochemical activation the same two peaks are found. A typical set of ALS voltammograms is shown in Figure 4. For the same quantity of electricity passed, these results illustrate the influence of the current density of the cathodic activation on the efficiency of the subsequent EP which lasted for 1 min. The ALSV marked Ni(1) corresponds to the electrode which was only activated by a cathodic deposition of 36 mC cm^{-2} of nickel at a current density of j_{act} = 18 mA cm^{-2}, but not subsequently subjected to an EP bath. The peak marked Ni(2) was also obtained for the electrode which was only activated, but this time by depositing a 40 times larger quantity of nickel at j_{act} = 72 mA cm^{-2} (cf. Figure 4, r.h.s. ordinate). It is seen that, even with a much larger quantity of Ni deposit, no change was found in the character of the peak.

By comparing the total of the charges of peaks (A) and (B) to that of peak Ni(1), an increase in the quantity of Ni obtained after 1 min of electroless plating equivalent to about 200 mC cm^{-2} can be estimated. The increase in charge occurs only upon activation at c.d.'s higher than 0.5 mA cm^{-2}. In contrast and in spite of the

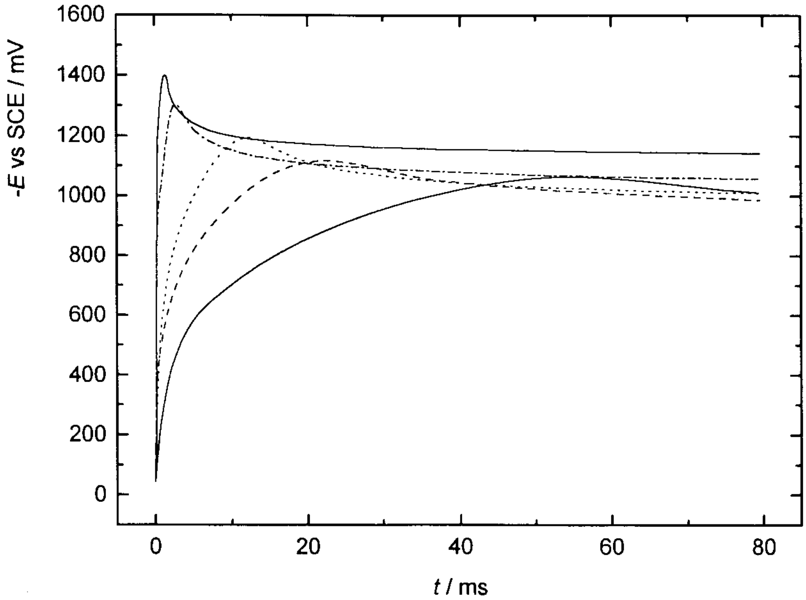

Fig. 1. Galvanostatic transients for the activation of EP at different current densities obtained for a glassy carbon electrode in a solution containing 0.1 M $NiSO_4$ and 0.5 M NH_4Cl (pH 8.7) at 40 °C. Current density, j: (——) 5, (– – –) 10, (- - - -) 20, (– · – ·) 50 and (——) 100 mA cm^{-2}.

fact that Ni is seen to have been deposited (cf. Figure 4, peak Ni(1)), total inactivity for EP (i.e., the same charge as cathodically deposited) is obtained upon activation at lower current densities. Also, total inactivity for EP is obtained if the activated electrode is not subjected immediately to the EP bath, but instead left out of the solution for over a minute.

The efficiency was determined by integrating the voltammograms of Figure 4 thus giving Figure 5. An abrupt rise in activity with c.d. is found in the c.d. region between 0.4 and 0.8 mA cm^{-2}.

Figure 6 illustrates the influence of the quantity of activating metal (Ni) on the efficiency of EP. This Figure was obtained in the same manner as Figure 5, except that the current density was fixed and the time of deposition varied. It can be seen that a sharp efficiency rise is again obtained, this time at a quantity of activating Ni corresponding to a quantity of electricity of about 8 mC cm^{-2}.

In some experiments the electroless Ni–P deposits, as well as those obtained electrochemically, were subjected to thermal treatment. As can be seen by comparing

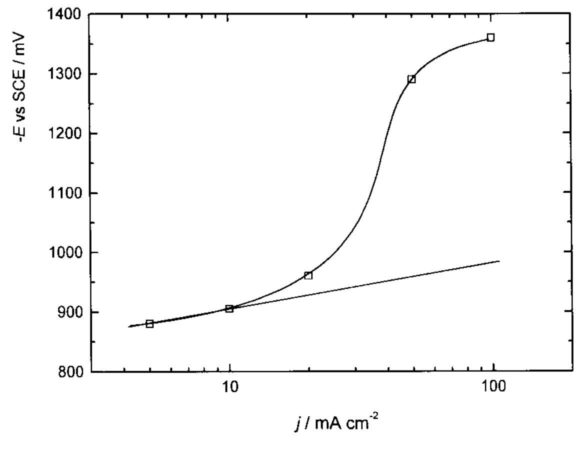

Fig. 2. Polarization curve pertaining to a stady-state attained after the activation pulses from Figure 1 reached charges of 1000 mC cm^{-2}.

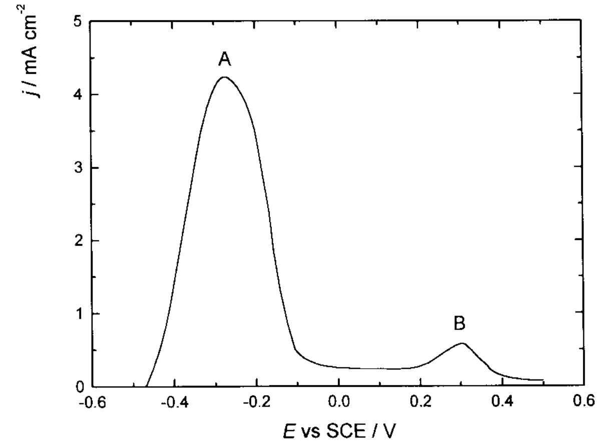

Fig. 3. ALSVs of a glassy carbon electrode obtained after chemical activation with Pd and 30 s of electroless Ni plating. $Q_{tot} = 216.1$ mC cm^{-2}; $Q_A = 195.5$ mC cm^{-2}; $Q_B = 20.6$ mC cm^{-2}.

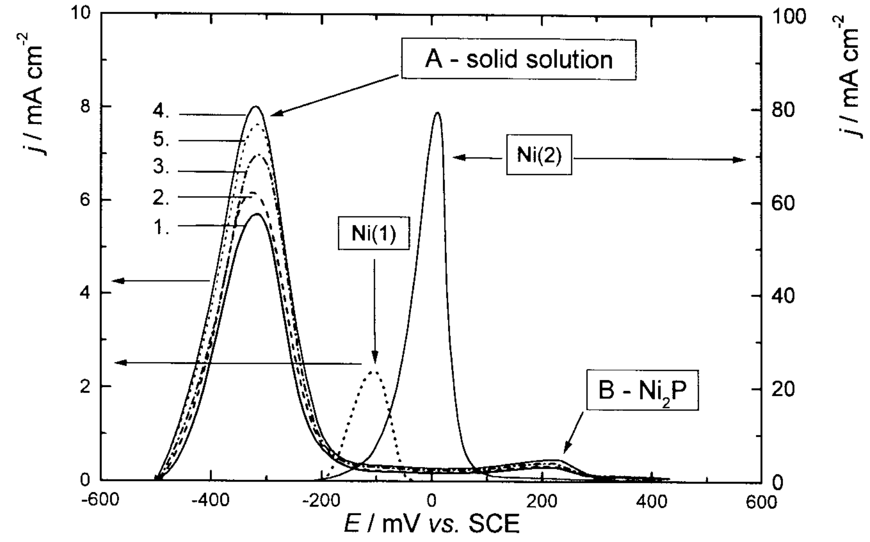

Fig. 4. ALSVs of glassy carbon electrodes activated for electroless plating by cathodic deposition of 36 mC cm^{-2} of nickel at different current densities. j_{act}/mA cm^{-2} = 0.72 (1); 1.8 (2); 18 (3); 90 (4) and 180 (5).

Figures 7 and 4, the thermal treatment did not affect the ALSV for pure Ni obtained electrochemically. In contrast, the ALSV recordings in Figure 7, pertaining to thermally treated EP samples, indicate significant changes in the phase structure of the deposit.

4. Discussion

It is well known that Ni, when deposited by electroless plating from a phosphorus containing bath (hypophosphite), includes some phosphorus in the metal, that is, a Ni–P alloy is formed [2–4, 6, 7]. This probably occurs due to some surface disproportionation of hypophosphite rendering phosphorus and phosphate. The phase diagram of metallurgically obtained Ni–P alloys is given in Figure 8 [6]. It may be seen that the solid alloy is a mixture of a solid solution of P in Ni and three different compounds in the eutectic mixture.

As seen in Figure 3 after chemical activation EP gives an alloy composed of only two phases. This may be explained by consulting the literature data on the phase structure of electroless Ni–P alloys [7]. Those obtained from alkaline baths (pH > 7) contain 3–7% of P, mostly

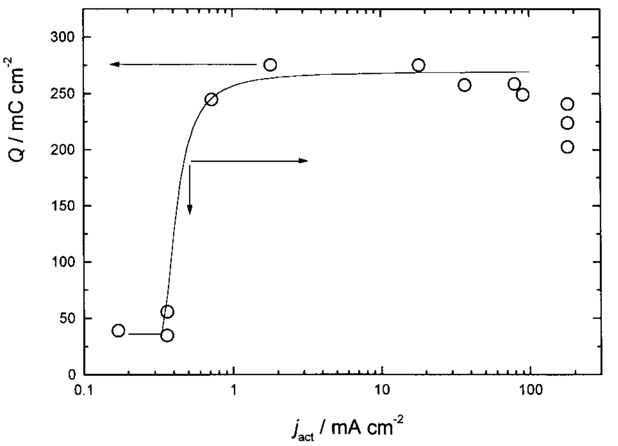

Fig. 5. Charge obtained during 1 min of electroless Ni deposition, upon activation of the process by cathodic deposition of one and the same quantity of Ni represented by the quantity of charge Q_{act} = 36 mC cm^{-2} at different current densities, j_{act}.

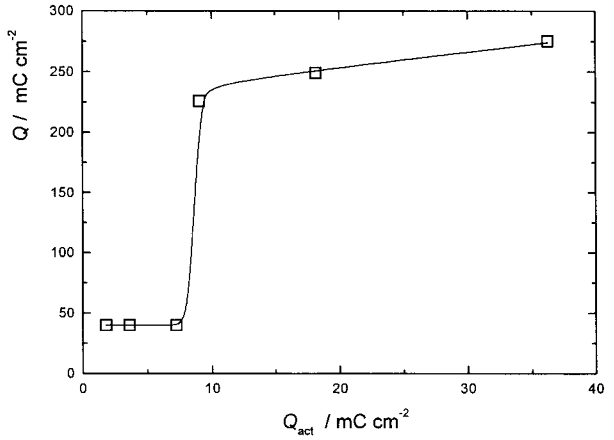

Fig. 6. Charge obtained during 1 min of electroless Ni deposition, upon activation of the process with one and the same current density j_{act} = 18 mA cm^{-2}, but different quantities of Ni represented by the quantity of charge Q_{act}.

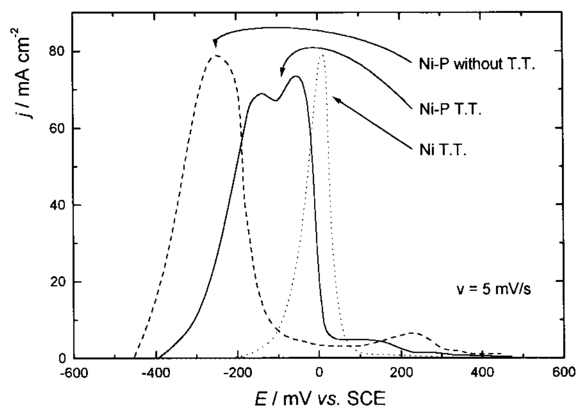

Fig. 7. ALSVs of electrodeposited Ni and of the EP deposit thermally treated for 2.5 h at $T = 300\,°C$.

as an interstitial supersaturated solid solution of P in a Ni hexagonal closely packed lattice, as well as some Ni_2P compound. Hence, the peaks are likely to reflect the presence of the solid solution (peak A) and the Ni_2P compound. The presence of Pd is not seen in Figure 3 because the total amount of Pd (about $50\,mg\,m^{-2} \cong 9\,mC\,cm^{-2}$ [8]) is so much smaller than the total charge of $216\,mC\,cm^{-2}$ under the ALSV, that it is buried in the curve pertaining to Ni–P.

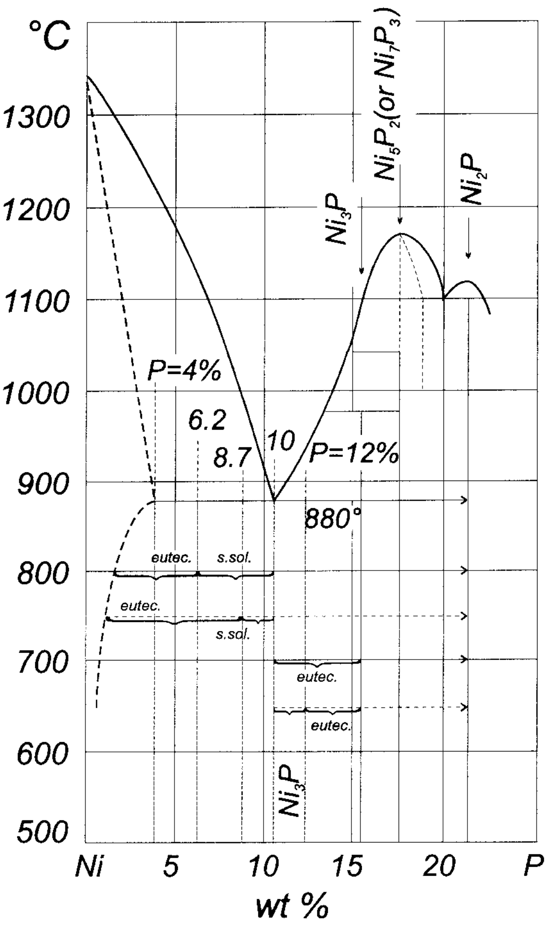

Fig. 8. Phase diagram of metallurgically obtained Ni–P alloys [6].

Electrochemical experiments show that the activation of a conducting surface for EP, carried out by the cathodic deposition of precursors, can also be successful.

However, such an activation is seen (Figure 5) to require an activation c.d. greater than a certain value ($0.5\,mA\,cm^{-2}$). Also, there must be a quantity of precursors at the surface, larger than a critical value (Figure 5), for a significant EP to take place within a given time. This is in accordance with electrochemical nucleation theory, whereby nucleation requires an overpotential larger than a critical value to reach a significant rate and produce a significant surface density of nuclei. Hence, the effect observed should be due to a large number of small active centres which are caused by an increased overvoltage in accordance with the theory of nucleation, compared with a small number of large grains obtained at low c.d. which do not activate the EP.

An interesting finding is that, for a certain c.d., an almost constant amount of the deposit is obtained within a certain time irrespective of the activation c.d. This is likely to be due to the fact that, during the period of activation, the substrate is already fully covered by a layer of Ni so that the surface available for EP does not increase by increasing the amount of the deposit.

The ALSV (Figure 4) shows that after some EP takes place, the phase structure of the deposit is significantly different from that obtained by electrodeposition in the nickel bath without hypophosphite (peak Ni(2)). The two peaks seen in the voltammogram are similar to those of Figure 3. Hence, the peak marked A should pertain to the dissolution of Ni and P from the solid solution, and that marked B should be due to the presence of nickel in the phosphide compound, Ni_2P.

The increase of the EP deposited metal with the quantity of metal obtained in the process of activation (Figure 6) exhibits a pattern similar to that of the effect of c.d. of activation (Figure 5) in that an abrupt increase is seen only after a certain quantity of the metal is cathodically deposited.

The initial value of Q corresponds to the quantity of Ni grains obtained by electrodeposition. Also, the subsequent slow linear increase in the total quantity of Ni obtained is not an increase in the efficiency of EP, but corresponds to an increase in the quantity of activating metal.

The results suggest that $8\,mC\,cm^{-2}$ are needed (and are sufficient) for subsequent efficient EP and that an excess of up to 36 mC cm^{-2} is superfluous, that is, it has no further effect. The excess is obviously used for enlarging the electrochemically formed grains prior to EP or reproducing the surface structure.

The effect of the subsequent thermal treatment is seen (in Figure 7) to consist of a significant shift in the major peak potential in the positive direction, as well as in the splitting of the peak.

The observed change is expected. It can be explained, on the basis of X-ray data, on the phase structure of the electroless Ni–P [9]. Upon treatment of this kind, the structure of the Ni–P alloy is known to change from a supersaturated solid solution of P in a Ni hexagonal closely packed lattice + Ni_2P to an interstitial solid solution of P in a β-Ni f.c.c. lattice + Ni_3P (Ni_5P_2).

The results in Figure 7 imply that the phase structure changes in the Ni–P alloys may be followed by ALSV, in a manner similar to that used in some earlier ALSV investigations of other binary alloy systems [5].

In conclusion, although electrochemical activation was proved to be successful, chemical activation has the advantage of providing an even distribution of the depositing metal over the entire substrate, while electrochemical activation is governed by the current distribution and, hence, may result in an uneven activation (e.g., in holes and recesses). However, by adjusting the bath so as to eliminate the effects of 'primary current distribution' (i.e., to govern the activation by the 'secondary' current distribution) evenness can be achieved over the entire substrate, except perhaps in deep holes.

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