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Electrochemical investigation of the autocatalytic deposition of Ni–Cu–P alloys

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Autocatalytic deposition of Ni–Cu–P alloys (55-65 wt % Ni, 25-35 wt % Cu, 7–10 wt %P) has been carried out. It is shown that the hypophosphite concentration must be higher than a certain threshold to induce the autocatalytic process. The impedance behaviour exemplifies the kinetic evolution: a large capacitive loop with a high-frequency inflection when only chemical displacement occurs and two well-defined capacitive features when the autocatalytic process is achieved. Mutual interactions occur between partial oxidation and reduction reactions which are both depolarized as compared to the separate reactions. In addition, phosphorus incorporation is always reduced when the copper content increases. A pH increase accelerates the plating process though it inhibits the cathodic discharge and reduces the copper content.

1. Introduction

Cupronickel alloys are known for their excellent corrosion resistance especially in marine atmospheres [1]. Conditions for the electrodeposition of Ni–Cu layers have previously been developed [2, 3] and their electrocrystallization kinetics investigated [4]. In the present work the electrochemical behaviour of the autocatalytic deposition of Ni–Cu alloys is reported. Few investigations have been carried out on the electroless deposition of ternary alloys [5–9].

The development of an appropriate electroless bath involves use of a reducing agent and complexing and stabilizing compounds, in addition to the metallic salts. As reducing agent sodium hypophosphite was chosen; this is widely used for electroless nickel plating [10, 11]. Formaldehyde is usually employed for electroless copper. Recently it has been pointed out that though copper does not catalyse the oxidation of hypophosphite, it can be deposited from these solutions in the presence of Ni^{2+} ions [12, 13].

Complexing agents are often added to improve bath stability [10]. For the Cu–Ni system it has been shown that a complexing agent is necessary to achieve the codischarge of the two metals which have two different deposition potentials [3, 4]; sodium citrate markedly shifts the discharge potential of copper and enables the deposition of Ni–Cu alloys. Citrate is also widely used for the autocatalytic deposition of nickel [10]. In addition it has been pointed out that citrate was the most appropriate complexing agent for electroless deposition of copper with hypophosphite; it leads to the highest plating rate [13].

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2. Experimental procedure

In a previous investigation a bath which deposits compact Ni–Cu–P alloy layers over a wide composition range was developed [14]. This contained 0.005 M copper sulphate, 0.0522 M nickel sulphate, 0.2 M sodium citrate and 0.15–0.6 M sodium hypophosphite. The pH was adjusted by ammonia in the range 8–10. Ammonium chloride or acetate (1 M) was added which enhances the plating rate and acts as pH buffer, increasing the bath stability. The temperature was held at $85 \pm 2°$ C. The solutions were deaerated by nitrogen bubbling.

The substrates were mild steel sheets. These were mechanically polished and chemically etched in dilute sulphuric acid prior to the experiment.

For the electrochemical investigation, rotating disc electrodes (nickel, mild steel or platinum) were used. The reference electrode was a saturated sulphate electrode (SSE), against which all potentials, corrected for ohmic drop, are referred. The counter electrode was a platinum sheet. Impedance measurements were carried out using a 1250 Solartron frequency response analyser coupled to a 1186 Schlumberger electrochemical interface and monitored by a microcomputer.

The chemical composition of the deposited alloys was determined by EDX analysis.

3. Results

3.1. *Polarization behaviour*

It is well known that the autocatalytic deposition of

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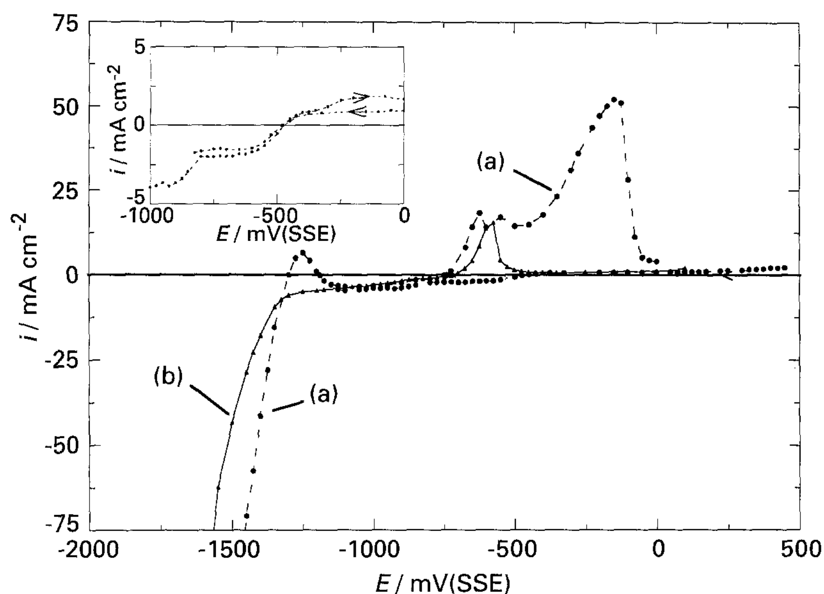


Fig. 1. Polarization curves recorded at 100 mV min^{-1}. Electrode rotation speed: 350 r.p.m. (a) Solution containing 0.46 M NaH_2PO_2, pH 9. (b) Solution without NaH_2PO_2, pH 9.

metals or alloys usually results from two half-reactions: anodic oxidation of the reducing agent, here sodium hypophosphite, and cathodic discharge of the metals. However, interactions often occur between these reactions [15, 16]. Cyclic voltammetry was carried out to characterize the various oxido-reduction processes.

As illustrated in Fig. 1 the deposition of the Ni–Cu–P alloys (curve a) occurs at potentials more negative than about −1.2 V. In the range −500 to −1000 mV, a small wave corresponds to the deposition of porous copper layers (see insert in Fig. 1). The anodic peak at −1.25 V corresponds to the oxidation of hypophosphite; it is not observed in solutions free of hypophosphite (curve b), nor on bare platinum. Two large oxidation peaks are observed in the complete solution (curve a) whereas only one, related to the dissolution of the Ni–Cu alloys, is observed in curve b. These curves may be related to the dissolution of a crystalline phase (peak at −650 mV) and an amorphous one (peak at −150 mV) as observed in the case of nickel, where it has been shown that the two phases may coexist [17].

The layers prepared, at the deposition potential, contain 31 wt % Cu, 60.5 wt % Ni and 8.5 wt % P for unmoved electrodes. When a cathodic polarization is applied the amount of incorporated phosphorus is slightly increased whereas the copper content is strongly reduced and the nickel content is increased. As previously observed for the electrolytic deposition of Ni–Cu alloys [4], Fig. 2 illustrates that, according to Brenner's definition [18], copper is preferentially deposited: the copper content in the deposit is always

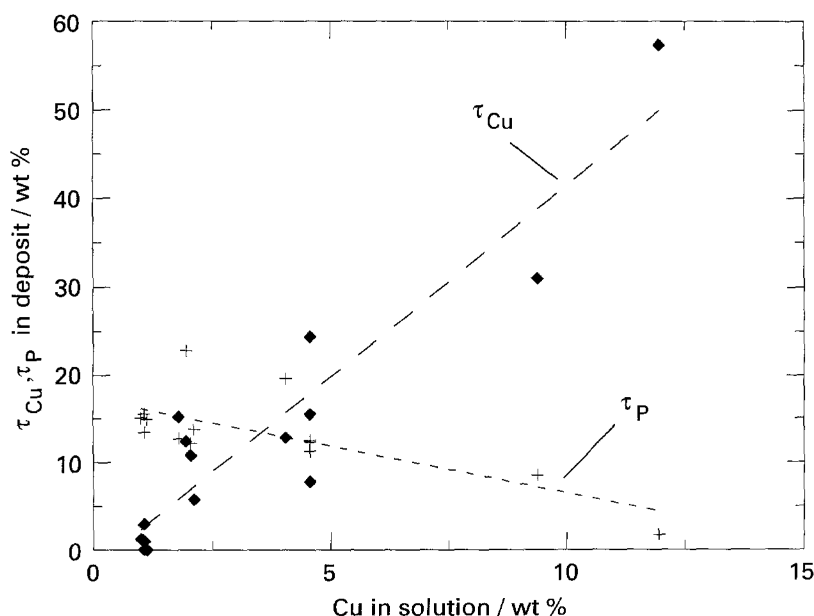


Fig. 2. Copper and phosphorus contents in deposits as a function of the copper per cent in the solution (unmoved electrode, pH 9).

much larger than in the solution (31 wt % Cu for the layers deposited from the solution containing 9.4 wt % Cu). In addition, the Figure indicates that copper and phosphorus contents change in an opposite way.

3.2. *Impedance behaviour*

Figure 3 shows the impedance diagrams recorded at various potentials. On bare platinum, at a deposition potential $E_d = -0.4$ V vs SSE, the polarization resistance is large and an inflection in the high frequency range is observed, which is characteristic of the formation of a porous layer (Fig. 3(a)). Indeed in the range 0.0 V to −0.9 V vs SSE, only thin copper layers, free of phosphorus or nickel, are obtained, probably by chemical displacement [14].

For potentials more negative than −1.2 V, i.e. at the deposition potential and in the cathodic polarization range, the impedance plots present several features. (i) The *high-frequency capacitive loop* is characteristic of the relaxation of the double layer capacitance in parallel with the charge transfer resistance, R_t. The

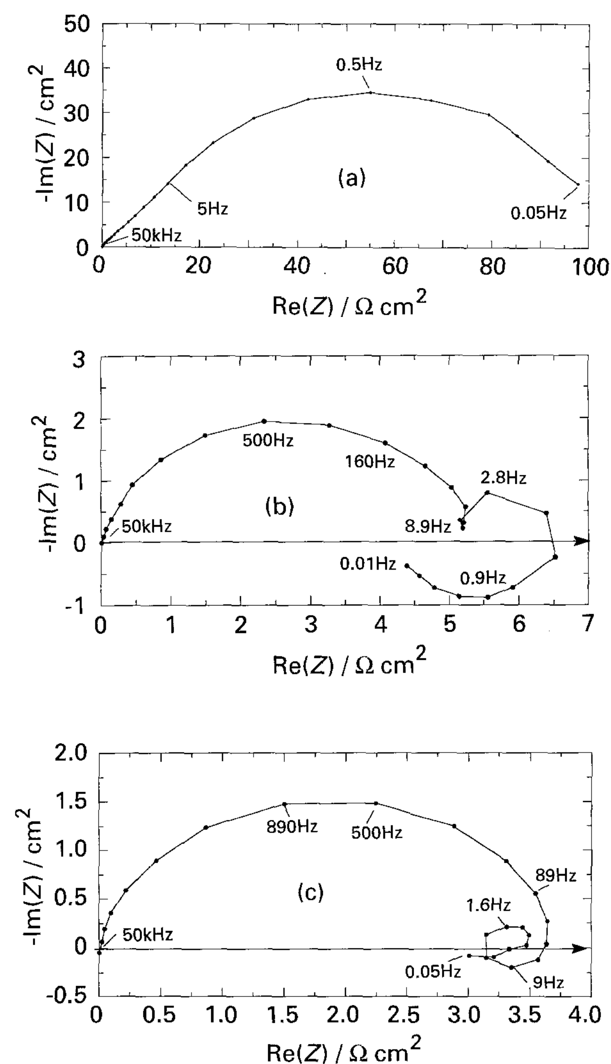


Fig. 3. Impedance diagrams recorded at various potentials. Electrode rotation speed: 500 r.p.m., pH 9. (a) Bare Pt disc at $E = -0.40$ V vs SSE. (b) $i = 0$ mA cm^{-2}, $E = -1.29$ V vs SSE (τ_{Ni}, 50 wt %; τ_{Cu}, 44 wt %; τ_P, 6 wt %). (c) $i = 20$ mA cm^{-2}, $E = -1.38$ V vs SSE (τ_{Ni}, 61.5 wt %; τ_{Cu}, 31.5 wt %; τ_P, 7 wt %).

magnitude of the double layer capacitance ranges between 50 and 150 μF cm^{-2}. For plating durations longer than 2 h it tends to increase and surface roughening is observed. (ii) An *inductive loop* with a characteristic frequency of about 8–10 Hz, is almost invisible at the deposition potential E_d (Fig. 3(b)). The size of the loop increases with cathodic polarization (Fig. 3(c)). This feature, which is always observed during the electrocrystallization of nickel, has been attributed to the two-step discharge of the Ni^{2+} ions via the adsorbed adion Ni^{I}_{ads} [4]. (iii) A *capacitive loop* in the medium frequency range, is very large at E_d (Fig. 3(b)). Its size decreases when the polarization increases, i.e. when the copper content decreases. (iv) A *lower frequency inductive feature* also occurs, which is often observed in the case of electrocrystallization of metals or alloys.

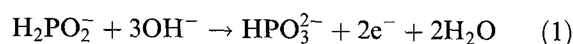
3.3. *Effect of hypophosphite concentration*

For concentrations below about 0.3 M the plating rate is very low (Fig. 4) and the deposition potential, E_d, is in the range −0.5 to −0.9 V. The P content is less than 2 wt %; the autocatalytic process has not started. When the hypophosphite concentration is increased, the incorporation of phosphorus strongly increases as well as the plating rate and E_d becomes more negative than −1.25 V.

Figure 5 shows, as already observed on the polarization curves in Fig. 1, that the presence of hypophosphite markedly depolarizes the cathodic processes. However a concentration increase of hypophosphite from 0.17 to 0.46 M does not significantly change the polarization behaviour. In the case of electroless nickel it has also been shown that hypophosphite or a reaction intermediate accelerates the discharge of nickel though the mechanism of interaction remains unknown [16].

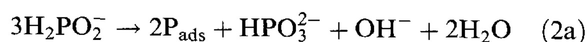
The impedance diagrams recorded at E_d (Fig. 6) illustrate the effect of hypophosphite concentration on the deposition kinetics. This clearly indicates that a concentration threshold is necessary to induce the autocatalytic process. For 0.15–0.3 M a very large capacitive feature is observed with a small high-frequency loop. For larger concentrations, the polarization resistance is markedly reduced and two capacitive features are observed which become better separated with increasing concentration (see also Fig. 3(b) for 0.46 M NaH_2PO_2).

Most of the investigations on the electroless deposition mechanism in hypophosphite solutions have been carried out in acidic media. In alkaline solutions [16, 19], according to Pourbaix diagrams [20, 21] the oxidation of hyphosphite leads to the formation of HPO_3^{2-} rather than $H_2PO_3^-$:



$$H_2PO_2^- + 3OH^- \rightarrow HPO_3^{2-} + 2e^- + 2H_2O \quad (1)$$

Incorporation of phosphorus would result from the disproportionation of $H_2PO_2^-$:



$$3H_2PO_2^- \rightarrow 2P_{ads} + HPO_3^{2-} + OH^- + 2H_2O \quad (2a)$$

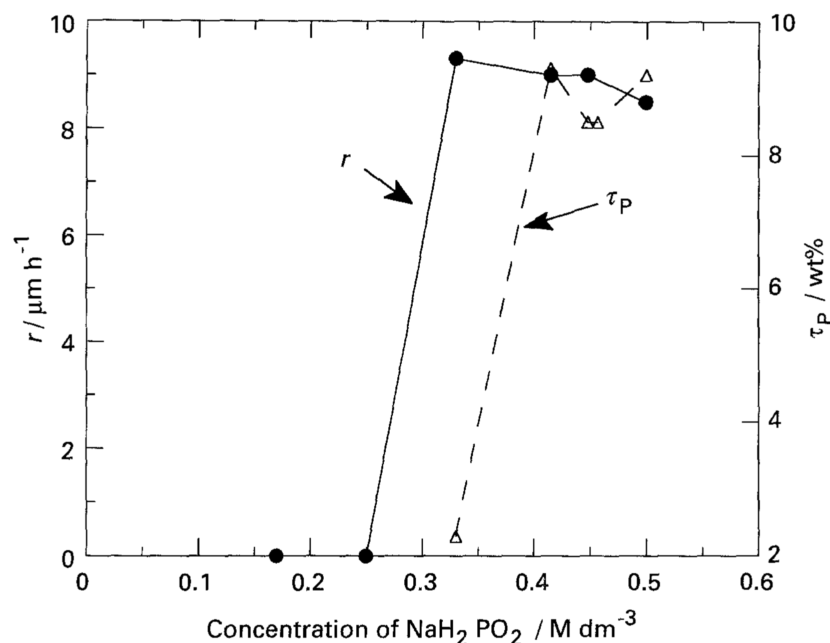
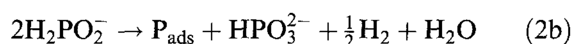


Fig. 4. Plating rate, r, and phosphorus content, τ_P, as a function of hypophosphite concentration for unmoved electrode, pH 9.

or



$$2H_2PO_2^- \rightarrow P_{ads} + HPO_3^{2-} + \frac{1}{2}H_2 + H_2O \quad (2b)$$

An investigation of the oxidation of hypophosphite carried out on gold electrodes indicates that it is a very sluggish process [19]. According to the authors, the P atoms produced adsorb on the electrode surface area and inhibit the oxidation. By contrast, during the electroless process the P atoms are incorporated into the growing layer, the oxidation is then depolarized.

As a decrease in both hydrogen evolution and pH is observed during the plating process, Reaction 2(a) most likely occurs. According to this reaction path, with increasing pH, the rate of hypophosphite oxidation increases and the amount of incorporated phosphorus reduces. Only slight changes in the phosphorus content are observed in the pH range 8–10, but, as expected from Reaction 1, the plating rate is accelerated when the pH is increased.

3.4. *Effect of electrolyte pH*

The solution pH has a great influence on the alloy composition and the plating rate [14]. For pH values lower than 8, copper rich layers are obtained with a very low rate. With increasing pH, the deposition potentials are shifted towards more negative values and the plating rate is enhanced. Figure 7 shows that the cathodic polarization curves are increasingly shifted towards negative potentials when the pH is increased from 8 to 10. This inhibition has a marked effect, especially on the copper content, which is

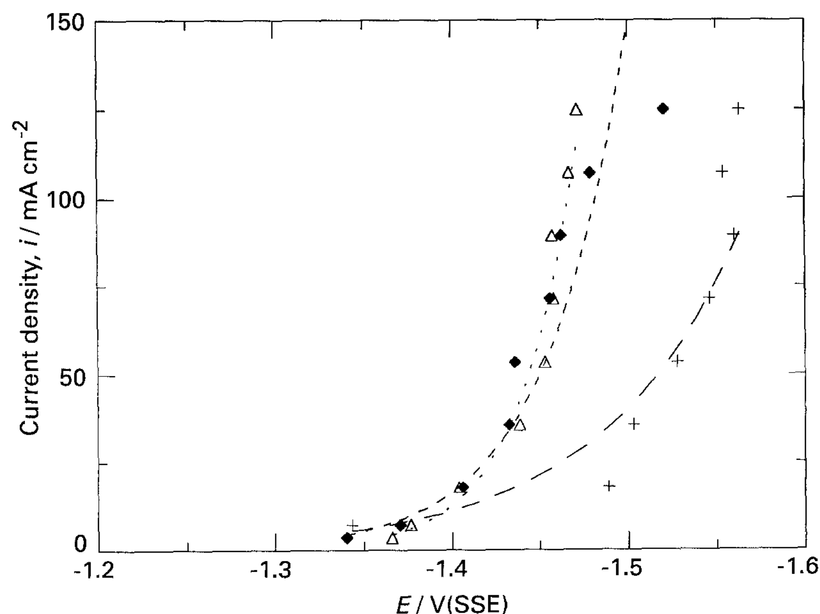


Fig. 5. Effect of hypophosphite concentration on the steady-state cathodic polarization curves. Electrode rotation speed: 500 r.p.m., pH 9. Key: (+) no hypophosphite; (◆) 0.17 M NaH_2PO_2; (△) 0.46 M NaH_2PO_2.

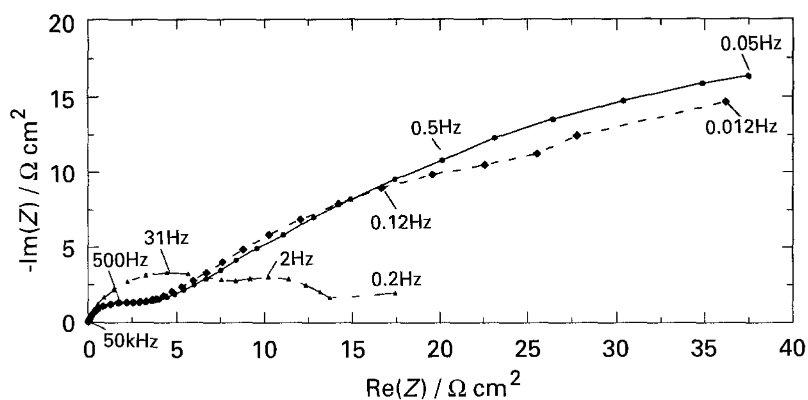


Fig. 6. Effect of hypophosphite concentration on the impedance diagrams recorded at the deposition potential. Electrode rotation speed: 500 r.p.m., pH 9. Key: 0.17 M (●) Ed = −0.5 V vs SSE; 0.25 M (◆) Ed = −0.8 V vs SSE; 0.33 M (▲) Ed = −1.3 V vs SSE.

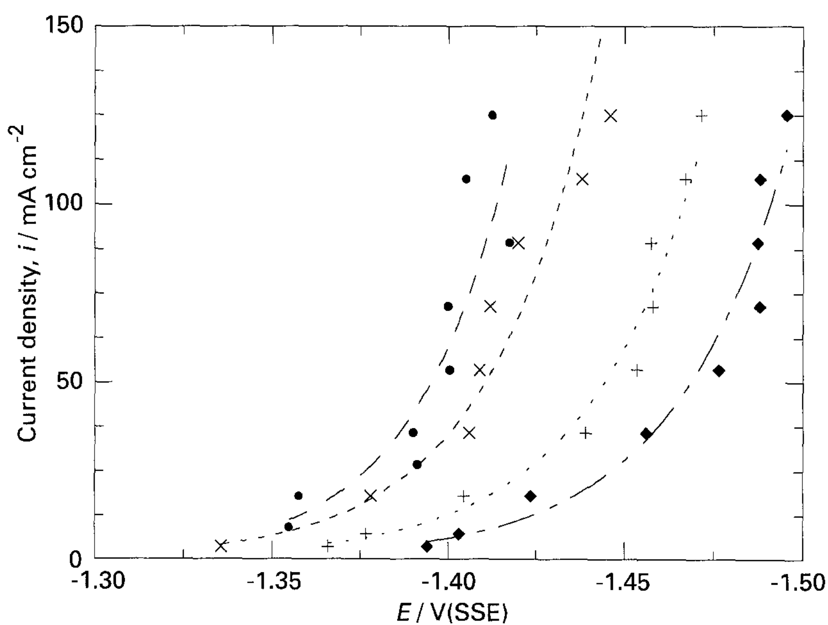


Fig. 7. Effect of solution pH on the steady-state cathodic polarization curves. Electrode rotation speed: 500 r.p.m., 0.46 M NaH_2PO_2. Key: (●) pH 8.2; (×) pH 8.6; (+) pH 9.0; (◆) pH 9.9.

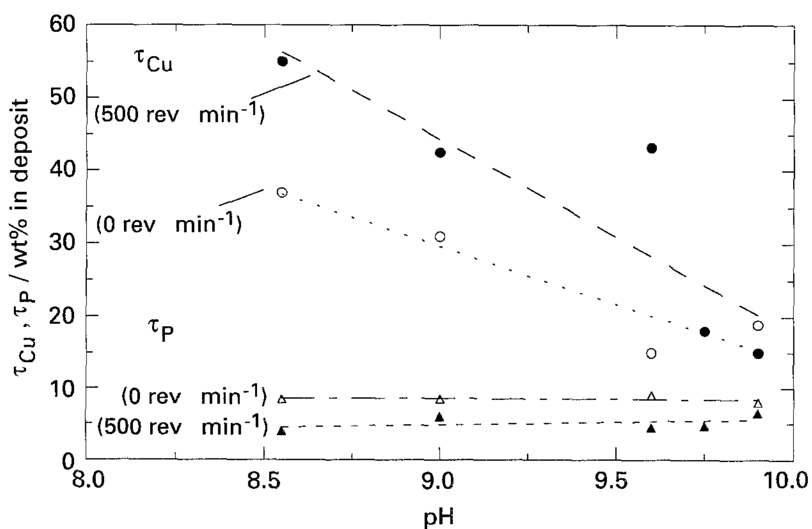


Fig. 8. Copper and phosphorus contents in the layers as a function of solution pH for unmoved and rotating disc electrodes. Key: (●) τ_{Cu}500 r.p.m.; (○) τ_{Cu}0 r.p.m.; (▲) τ_P500 r.p.m.; (△) τ_P0 r.p.m.

drastically reduced when the pH is increased from 8.5 to 10 (Fig. 8). Indeed the stability of the citrate complexes is enhanced in alkaline solutions, especially that of copper complexes [22]. As a consequence their discharge is inhibited as already shown in the case of electrodeposition [23]. The amount of incorporated P changes only slightly. The Figure also points out that the copper content increases with electrode rotation speed, indicating that its discharge is partly controlled by diffusion due to the low bulk copper sulphate concentration. An opposite trend is observed for the P incorporation. As already shown in Fig. 2, it appears that a negative interaction between copper and phosphorus contents exists.

4. Conclusion

Conditions for the autocatalytic deposition of Ni–Cu–P alloys have been determined. Interactions between anodic and cathodic processes have been pointed out: both reactions are depolarized. The autocatalytic process occurs for open-circuit potentials more negative than about -1.2 V vs SSE. Indeed copper, whose deposition potential is much more noble than nickel, even in citrate solutions [4], cannot catalyze the oxidation of hypophosphite [8, 12]. The deposition potentials, resulting from the anodic and cathodic reactions must be sufficiently negative to allow the codischarge of nickel. If this condition is not fulfilled, only thin copper layers are obtained which do not contain phosphorus or nickel. The evolution of the impedance diagrams exemplifies the kinetic changes: large and depressed capacitive loops with high-frequency inflection for E_d less negative than -1.2 V vs SSE. As soon as the autocatalytic deposition starts, two capacitive features are observed. The charge transfer resistance is an estimation of the deposition rate.

A threshold of hypophosphite concentration is necessary to induce the autocatalytic process. The molar ratio of [Hypophosphite/Ni^{2+}] must be larger than 6. It is markedly higher than in electroless nickel, for which a ratio of 3 is usually employed [10, 11, 16] but not as high as for the copper solutions which contain only traces of nickel (ratio larger than 10) [12].

Copper is always preferentially deposited, its content in the deposited alloy is much larger than in the solution. Its discharge is partly controlled by mass transfer and is markedly inhibited with increasing pH. In addition it seems that there exists interactions between its discharge and the phosphorus incorporation reaction: phosphorus and copper contents always change in a reverse way.

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