

On the Mechanism of Electroless Ni-P Plating

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ABSTRACT

The electroless deposition mechanism of nickel, in a chloride-based solution, using hypophosphite ion as reducing agent was examined using potentiodynamic method and open-circuit potential measurements. The results indicate that the mixed potential theory is unable to describe this system. This is due to the nature of the involved mechanism. It is assumed that the process is initialized by adsorption of hypophosphite ions, followed by the homolysis of primary reductant species, resulting in the formation of atomic and ionic radicals which promote nickel and hypophosphorous acid reduction to originate the Ni-P deposit. The initial deposition stages of Ni-P were observed, revealing that the substrate induction, which leads to an increase in the catalytic activity, is not related to a galvanic displacement process, but rather to the establishment of the electrochemical conditions which allow the adsorption/breakdown of the hypophosphite ions. The experimental results are in good agreement with the proposed mechanism.

Although electroless deposition of nickel from hypophosphite solutions, first described by Brenner and Riddell,¹ has been extensively studied,²⁻⁹ the involved mechanism is still subject of controversy.¹⁰⁻¹² This is due to the lack of knowledge on the electrochemistry of the oxidation of the reducing agent over a catalytic surface,¹³ the main source of disagreement among the authors.¹⁴⁻¹⁸

Another point of discussion is the ability of the mixed potential theory,¹⁹ for independent partial reactions, to describe the electroless process. There are authors who claim its validity,²⁰⁻²² while others points out the interdependence features of the partial reactions.²³

On the other hand, the behavior of the reducing agents present some particular features depending on its nature, which makes a unified view of the phenomenon difficult; however, there are attempts to present a universal mechanism for all reducing agents used in the electroless plating process.²⁴

To discuss the autocatalytic deposition of nickel accompanied by phosphorus incorporation in the film it is important to know the effect of the operating parameters such as the substrate nature, pH, temperature, reactants concentration, on the properties of the obtained deposit in order to clarify the role of each one in this peculiar process of metallic deposition. Nevertheless, it becomes critical to understand the first steps of the process which are determinant for the development of the electroless process. It is widely known that the hypophosphite ion adsorbs easily on an adsorbing hydrogen catalyst in order to oxidize, producing the more stable phosphite anion.¹³ Several workers studying this reaction have concluded that the mechanism proceeds by homolysis of the hydrogen bond of the reducing agent with radicals formation.^{4,6,15,24-28} Moreover, kinetic and computational simulation studies on the formation and reactivity of the hypophosphite-based radicals^{29,30} pointed out the occurrence of an anionic radical in addition to the hydrogen radical. However, if it is widely believed that the nickel reduction proceeds by hypophosphite-based radicals oxidation, the phosphorus co-deposition mechanism is not yet explained in a way supported by experimental data.

In this paper, particular attention is given to the initial stages of the electroless process using sodium hypophosphite as the reducing agent, in order to understand the interactions and reactions which lead to the deposition of Ni-P.

Experimental

Working electrodes were constructed from Johnson-Matthey "Specpure" copper and nickel rod sealed with epoxy resin in "Kel-F" holders. The exposed cross section (0.196 cm² geometric area) was polished to a mirror finish on 6 μm diamond paste and aqueous suspension of successively finer grades of alumina down to 0.05 μm; for each experiment a fresh surface was generated by hand polishing with 0.05 μm alumina.

The working electrode was mounted in a double-wall three-electrode cell with a platinum foil counterelectrode. Electrode potentials were controlled with respect to the saturated calomel electrode (SCE) by an EG&G Princeton Applied Research (PAR) Model 273 potentiostat/galvanostat.

The experiments were carried out at 50.0 ± 0.1°C by circulating thermostated water through the double wall of the cell.

Current potential relationships were collected by a Houston Omnigraph Model 2000 X-Y-t recorder or through a PC-IT Sperry computer equipped with PAR 270 interactive software.

For the electroless Ni-P deposition experiments a commercial copper foil with 70 cm² exposed area was used as the substrate and a commercial aluminum wire as the inducer. The substrate surface/solution volume ratio was always kept under 250 cm² dm⁻³. Previous experiments have shown that up to 500 cm² dm⁻³ that relation had no significant influence either in the rate of deposition or in the deposit phosphorus content.

Electrolyte solutions were prepared from "Analar" grade chemicals and deionized bi-distilled water. They were thoroughly deoxygenated directly in the cell, prior to measurements with N₂ (99.999%), and an inert gas atmosphere was always kept over the liquid surface.

Unless otherwise stated, the solutions containing 0.126 mol dm⁻³ NiCl₂, 0.142 mol dm⁻³ NaH₂PO₂, and 0.561 mol dm⁻³ NH₄Cl (solution A) and 0.150 mol dm⁻³ NiCl₂, 0.150 mol dm⁻³ NaH₂PO₂, and 0.500 mol dm⁻³ NH₄Cl (solution B) were used.

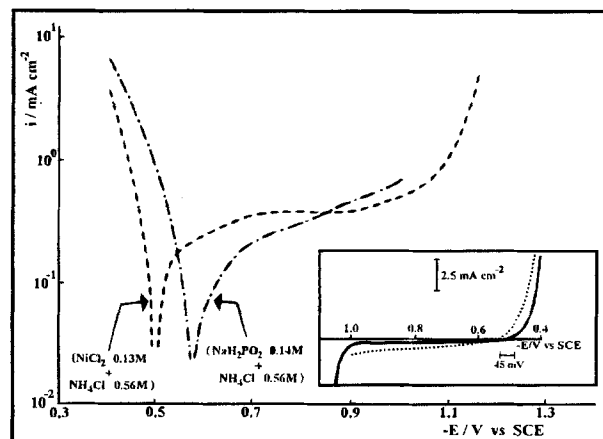


Fig. 1. Anodic and cathodic polarization curves on copper electrode at 50°C. It includes the real i vs. E profile (—) obtained with the complete solution and the calculated one (---) according to the mixed potential theory, $\nu = 10$ mV/s.

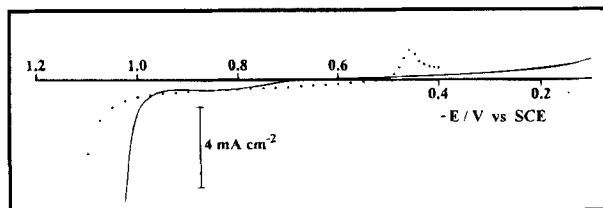


Fig. 2. Sum of the anodic and cathodic polarization curves, obtained on the nickel electrode in the same solutions as in the Fig. 1 (.....) and experimental curve obtained in the complete solution (—).

The phosphorus content in the deposit was determined by energy dispersive x-ray spectrometry (EDS) using a Tracor Northern TX1/50-6618 coupled to a scanning electron microscope Jeol JSM-T 300.

The structural thin film analysis was made by x-ray diffraction. It used a Philips diffractometer with a high power generator, operating at 50 kV and 40 mA.

Results and Discussion

According to the Wagner and Traud,¹⁹ theory of mixed potentials, the rate of a faradaic process is independent of other faradaic processes occurring simultaneously at the electrode and thus depends only on the electrode potential. If the electroless metal plating were to behave as a mixed potential system, the polarization curves for independent anodic and cathodic processes, when added, will be able to predict the overall rate of deposition and the onset potential for the electroless system under study.

Figure 1 presents the anodic and cathodic polarization curves on a copper electrode obtained from an electroless solution in the absence either of nickel ions or reducing agent, respectively. It can be also seen in this figure that the sum of partial contributions do not reproduce the experimental polarization curve obtained in a complete solution. The predicted onset potential for electroless deposition differs *ca.* 45 mV from the real one.

The same main feature was observed when using a nickel electrode, Fig. 2. It must be pointed out that an electroless experiment carried out in the same conditions as cited for Fig. 2, develops with a rate of electroless Ni deposition (measured by the weight gain method) more than one hundred times higher than the predicted rate by mixed potential theory; thus, the Wagner-Traud theory is unable to describe the process.

The failure of the mixed potential theory applied to this system cannot be ascribed only to the fact that the two partial reactions in electroless plating are not entirely independent but mainly because the reduction of metal ions involves many more electrons than those provided by the anodic partial reactions.

In order to clarify which species are responsible for the reduction of the metal ions, a careful analysis of the initial stages of the electroless deposition is essential. Since the autocatalytic deposition is an electrochemical process in nature, the obvious parameter for following the reaction is the electrode potential, whose variations reflect the chemical and structural changes occurring in the double layer region.

For the kinetic and thermodynamic feasibility of an electroless process, the adsorption of the reducing agent on the substrate surface must occur in order to promote their oxidation. The materials able to give rise to this interaction are the so-called catalytic materials;¹³ nickel, cobalt, and palladium are examples of systems containing the hypophosphite ion.^{2,31,32} Nevertheless, the Ni-P electroless process may occur on other substrate materials under given conditions: noncatalytic materials like stainless steel,³³ can become active under suitable temperature; on others, such as poorly noble materials, *e.g.*, Al, Fe, Zn, the nickel deposition is initiated by galvanic displacement giving rise to catalytic surface on which, thereafter, the electroless process develops; also the electrode potential of the noncata-

lytic substrate can be shifted to more negative values by short-circuiting a poor noble metal for a short period. When the last process is used to promote the electroless deposition it is referred to as induction.²³

The potential profiles observed for the beginning of the deposition process over a wide pH range, using a copper electrode in an electroless bath are displayed in Fig. 3. A few seconds after the immersion of the substrate in solution, a stable potential value, characteristic of this system is established. At this point there is no metallic reduction since the copper itself is unable to promote the adsorption of the hypophosphite ion. To reach the deposition potential, the substrate was induced by connecting an Al foil. When the peak potential is reached, a fair amount of hydrogen evolution can be seen both on the copper electrode and on the Al inducer. The actual potential is characteristic of the Cu/Al system in this solution. After disconnecting the aluminum wire, the electrode presents a potential which can be ascribed to the system Ni-P/electroless solution at a given pH and temperature. Figure 3 shows that, in the alkaline region, the rise of the electrode potential after induction is not linear as it is in the acid range, but bends before the potential peak. Besides, in the acid region, the potential value obtained by induction is always more negative than the onset potential of electroless deposition whereas at high pH values it is not clear if the peak potential is due to induction or results from the occurrence of a determining step in the mechanism of electroless Ni-P deposition. Additionally, the time lapse between the induction and the instant in which the peak potential is reached increases with the pH up to a certain value and decreases thereafter. The same features were observed when solutions containing one more complexing agent (citrate ion) and one more depolarizing agent (acetate ion) were used. These observations are relevant since they do not support the theory that predicts the induction process as a galvanic displacement.

Experiments with induction carried out under stirred conditions, Fig. 4, clearly show that to reach the onset potential for electroless metal deposition, a galvanic displacement process is not necessarily involved. As depicted in the figure, the stirring of the solution promotes a slight increase, in the cathodic sense, of the copper electrode potential. When the Al contact is made, a fast increase of electrode potential occurs followed by a region of slow change reaching a plateau where neither hydrogen evolu-

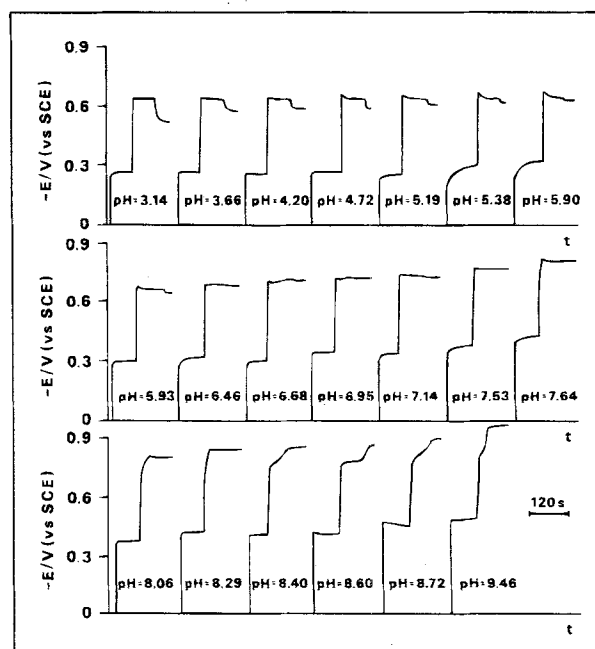


Fig. 3. Potential profiles at the beginning of the deposition process using a copper electrode induced with an Al wire for a period of *ca.* 60 s in the solution A.

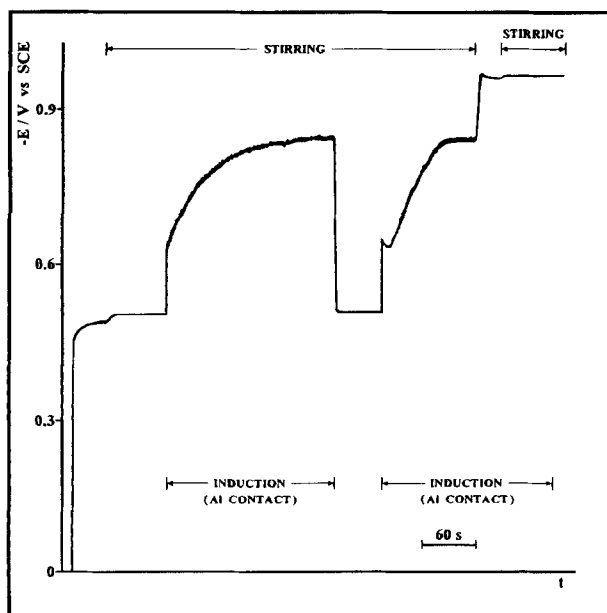


Fig. 4. Stirring effect in the initial stages of electroless metal deposition on copper induced by Al in the solution A at pH 9.2 adjusted with NH_4OH .

tion nor nickel deposition is observed. The drop of the electrode potential to the characteristic value of the interface copper/stirred solution when the Al inducer is disconnected, gives evidence that the electroless potential was not reached and that nickel reduction over the copper electrode by galvanic displacement did not take place. A second induction attempt in the stirred solution reveals basically the same features, but the cessation of solution stirring leads to the establishment of the necessary conditions for electroless deposition to occur, and the electrode acquires a potential value which can be ascribed to the Ni-P/electroless solution interface. After this, the restart of stirring or the removal of the inducer cannot interrupt the deposition process. These observations reveal that the induction mechanism is composed for at least two steps, the first one being kinetically affected and the second hindered by the electrolyte movement. However, none of them involve a galvanic displacement (one that is not hindered by stirring). Therefore the adsorption and oxidation of the reducing agent take place over copper, a noncatalytic material, when the substrate is connected to a less noble metal.

The absence of a galvanic displacement during the induction process suggests that the mechanism for reaching the potential value which reflects the establishment of conditions for observing the oxidation of the reducing agent, does involve the hypophosphite anion but not the nickel cation, even if the process takes place in a noncatalytic substrate under induction. Actually, the potential profiles of a nickel electrode immersed in a solution in the absence of nickel ions, Fig. 5, are quite similar to those obtained in a completely electroless solution. It can be seen in this figure that when a nickel electrode is immersed in a hypophosphite solution, it takes some time, transition time, to establish the interactions that lead to the anion oxidation, revealing that it is feeble catalytic material under these operating conditions. Nevertheless, the substrate is able to create the interactions with the reducing agent in order to promote their oxidation, which is visually confirmed by fair hydrogen evolution on the electrode. However, the transition time can be reduced by induction with an appropriate material (Fig. 5b), being the final potential the same as observed in the noninduced experiment (Fig. 5a); the occurrence of the same electrode process can be assumed. It is worthwhile to note that the magnitude of the final displayed potential, ascribed to the oxidation of hypophosphite ion, is appropriate to promote the reduction of nickel ions (when present). Indeed, in a completely electro-

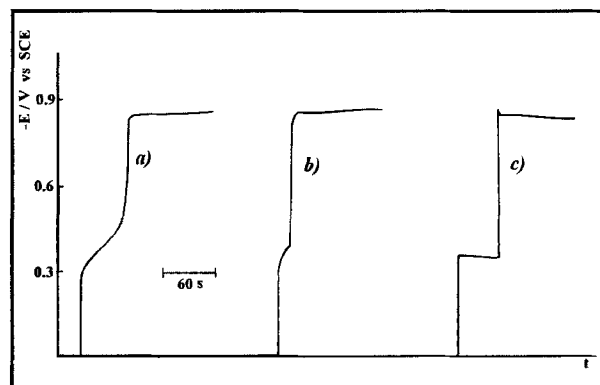


Fig. 5. Potential profiles of a nickel electrode in a solution containing $0.15 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_2 + 0.50 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$ (pH 7.00): (a) spontaneous process, (b) induced, (c) with $0.15 \text{ mol dm}^{-3} \text{ NiCl}_2$ (pH 8.30 adjusted with NH_4OH), induced.

less solution, nickel reduction is observed at this potential, even at higher pH value (Fig. 5c). It can be concluded that the required conditions for the electroless process to take place, are accomplished by a mechanism involving exclusively the reducing agent and the substrate; the process can be catalyzed by means of induction with a suitable material.

In agreement with the above mentioned observations, we suggest that during the transition time, the adsorption of hypophosphite and the homolysis of the hydrogen bond with the production of hydrogen radicals occurs. This step takes place spontaneously over a catalytic material or over an electrolessly inactive substrate whose potential was shifted to more cathodic values than its open-circuit potential in the electroless solution. The process of potential displacement can even be used with catalytic substrates in order to minimize the transition time as schematically shown in Fig. 6, assuming the hypophosphite adsorption by means of both hydrogens.¹³

Therefore, the main reactions will be expressed by the following equations

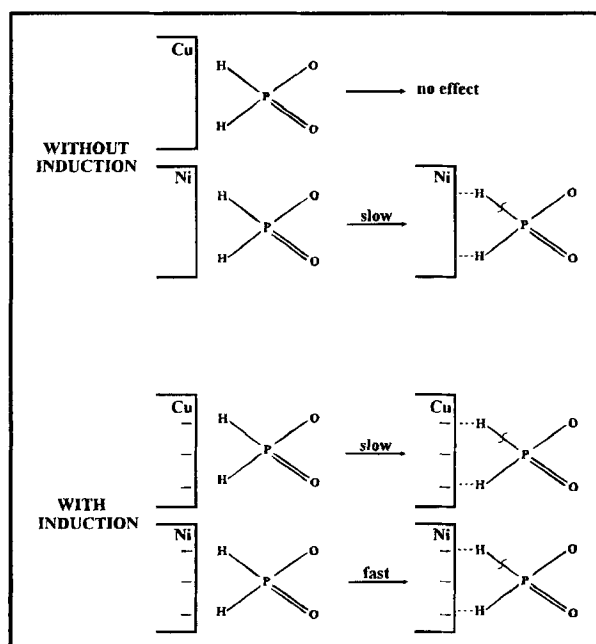
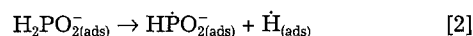
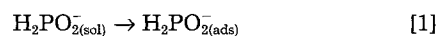


Fig. 6. Scheme of the initial steps of the electroless nickel deposition over catalytic and noncatalytic materials with and without induction.

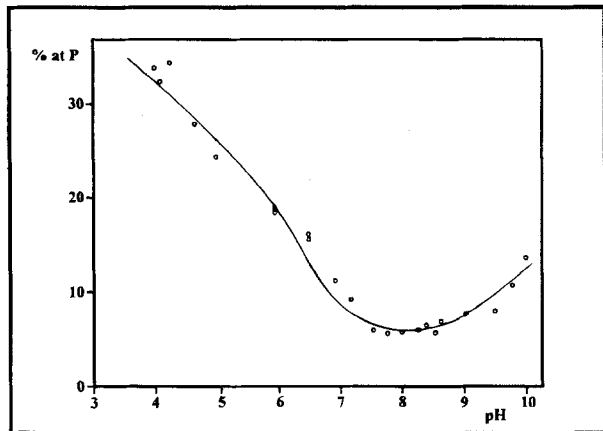
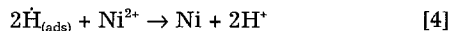


Fig. 7. Phosphorus content in the Ni-P electroless film, obtained in solution B over a wide range of pH adjusted with NH₄OH.

The combination of two hydrogen atoms will be responsible for part of the observed gas evolution



as well for nickel ion reduction, if present, in some extension



The mechanism expressed by Eq. 1 to 4 explains the occurrence of hydrogen evolution over the substrate in a solution containing only sodium hypophosphite, as well the difference between the amount of nickel deposited in an electroless experiment when compared with the current developed by the anodic oxidation of hypophosphite ions in a solution in the absence of nickel ions under the same experimental conditions. In fact, the reduced metal mainly results from the direct reaction among the nickel ions and the reductant radicals rather than from the consumption of the electrons produced by the anodic oxidation of the reducing agent, this being the main reason of the failure of the mixed potential theory.

The other radical, H $\dot{P}O_2$, will oxidize with the formation of atomic hydrogen or, depending on the experimental conditions, give rise to an anodic current.

The resultant electrons from the oxidation of the H $\dot{P}O_2^-$ radical, are responsible to some extent for the reduction of the metal and the hydrogen ions according to



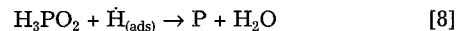
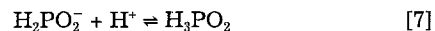
Simultaneous with the nickel reduction, in an electroless experiment using the hypophosphite ion as the reducing agent, there is always phosphorus codeposition producing an Ni-P film. Typically the amount of nonmetallic element in the alloy can vary between 3 and 35 atom percent (a/o), depending on the experimental conditions.³⁴ This quantity is strongly dependent on the solution pH, and it is usually reported as increasing with acidity.^{35,36} Under the experimental conditions used in this work (where only NH₃ acts as complexing agent), it shows the expected evolution up to pH 8, but for the range 8 to 10, an increase of the amount of phosphorus in the deposit with the alkalinity is observed as displayed in Fig. 7.

The crystallinity of the obtained films also reflects this feature. Usually, the crystallinity increases with the pH due to the decrease of foreign atoms in the metallic matrix. However, in the present case, this behavior is only observed for deposits prepared in the more acidic region, since the degree of amorphicity of the film is important, owing to the increase of the phosphorus content, when pH values above 8 are considered, as illustrated in Fig. 8.

Although this abnormal behavior can be easily ascribed to the presence of ammonium ions in high concentration in

the electroless solution, it is very helpful for understanding of the phosphorus co-deposition mechanism.

Phosphorus is a result of the reaction between the hypophosphorus acid with a hydrogen radical



Equations 7 and 8 explain satisfactorily the decrease of phosphorus content with the alkalinity by means of the equilibrium displacement of reaction 7 to the left side, but they cannot explain the change in this behavior after a certain pH value. However, the presence of ammonium ions is determinant for the amount of available species to the reduction process. In a solution containing nickel and ammonium ions, the following equilibria must be considered



with the production of species ([Ni(NH₃)₆]²⁺) which requires a higher activation energy to be reduced than the Ni²⁺ ions.

According to reactions 7 and 9, at low pH values, there is a significant concentration of hypophosphorus acid and a low concentration of NH₃; thus, the extent of phosphorus formation (reaction 8) is important as well as the nickel reduction which is not favored by the low pH (reaction 4)

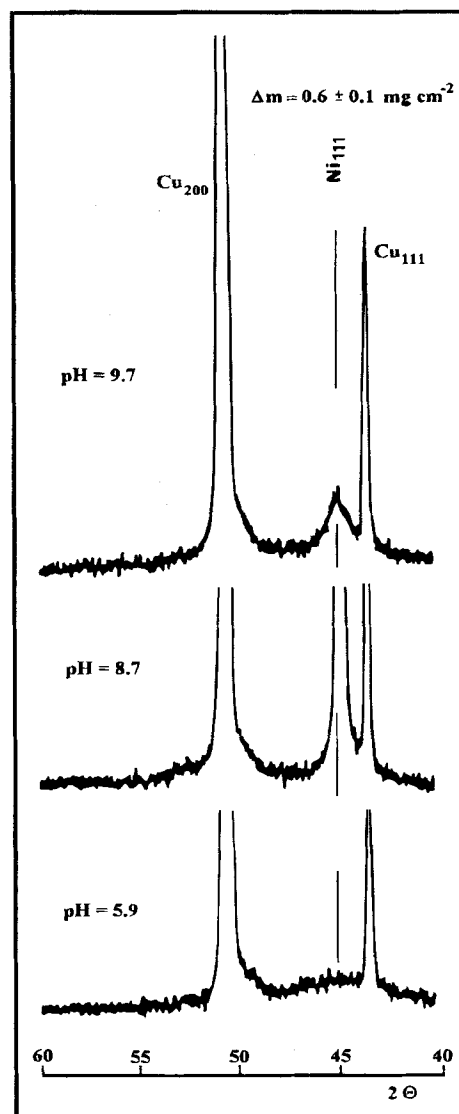


Fig. 8. Diffractograms of Ni-P thin films over copper substrate, deposited by the electroless process in solution B at different pH values adjusted with NH₄OH.

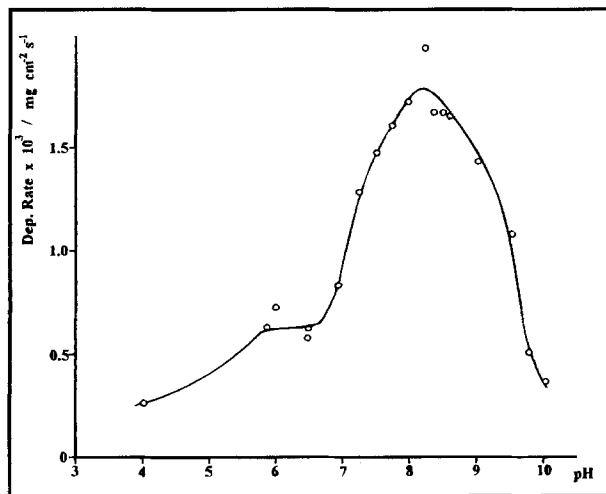


Fig. 9. Rate of electroless Ni-P deposition in solution B at different pH values adjusted with NH_4OH .

but is mainly due to the high concentration of free nickel ions in solution.

At medium pH values, the hypophosphorus acid concentration is relatively low and a medium concentration of free nickel ions is present. As a result, the ratio of phosphorus to nickel in the deposit is very low, as is observed.

On the other hand, for strongly alkaline solutions, the concentration of both hypophosphorus acid and free nickel is very low (reactions 7, 9, and 10). Due to the lack of both oxidant species, the ratio of phosphorus to nickel in the deposit is significant, and the overall rate of deposition is low. The dependence of the deposition rate on the pH is shown in Fig. 9, confirming the predictions of the proposed mechanism.

Conclusions

In electroless nickel deposition, using the hypophosphite ion as the reducing agent, the first step of the mechanism is the adsorption of the reductant species and the homolysis of its hydrogen bond with the formation of radicals. This step can occur spontaneously over the so-called catalytic substrates, which are the materials able themselves to establish the interaction with the hypophosphite ion in order to promote the cleavage of the hydrogen bond, or over induced noncatalytic materials. The mechanism of the induction with a less noble metal does not involve a galvanic displacement step but rather a negative shift of the electrode potential which allows the adsorption and homolysis of the reducing agent.

The radicals formed in the first step are mainly responsible for hydrogen evolution on the electrode as well as for the metallic alloy deposition. However, there is anodic oxidation of the resulting radicals to some extent which contributes to the overall hydrogen and nickel reduction.

This mechanism explains why the mixed potential theory is unable to elucidate this process. Actually, most of reduced nickel is a result of the reaction of its ions directly with the reducing radicals. This process involves a current which is not measurable in the electrochemical oxidation of hypophosphite ion which, in our experimental conditions, represents less than 1% of the real charge-transfer taking place in the electroless experiment.

The phosphorus co-deposition results from the reaction between the hypophosphorus acid and the radicals generated from the hypophosphite homolysis. The phosphorus content in the deposit decays with the increase of the pH just to a value of pH 8 in our experimental conditions and begins to increase after this pH. This phenomenon is ex-

plained on the basis of the removal of free metallic ionic species in the ammonium ion-containing solution owing to its coordination to form stable amino-complexes at high pH values.

An electrochemical study of the auto-oxidation of hypophosphite ion over a catalytic material is in progress in order to achieve a better understanding of the involved mechanism of electroless deposition using this reducing agent.

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