Investigation of acidity and composition of the bath deposition in electroless Ni-P alloys with ammonium acetate as accelerator in acidic medium.

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Abstract

This paper has studied systematically the acidity, the composition bath when the ammonium acetate as accelerator in acidic medium and its effects on the deposition rate, P content, morphology and structure of electroless Ni-P. It has been found that the deposition rates increase and approach a maximum value with the decrease of pH values of the bath. The evolutions of acidity of the bath affect the morphology and the structure of the Ni-P deposit. Indeed, the investigated of the deposition rate of electroless Ni-P deposits as function the acidity using cyclic voltammetry proved the increase of the oxidation of H2PO2- with the decrease of the acidity of the bath. Besides, the deposition rates decrease and approach a maximum value with increase in the in the concentration of nickel sulfate, sodium hypophosphite and pH value, respectively. However, the deposition rates only decrease with increase in the sodium citrate. Indeed, when the report molar [Ni2+]/[ H2PO2-] is destabilized and different from at 0.52 or the acidity of the bathe is very acidic, the decomposition spontaneous of the bath is observed.

Keywords: Electroless Ni-P; pH and composition effect; Morphology; Structure.

1. Introduction

The electroless nickel (EN) process is undoubtedly the most important catalytic plating process used to solve materials problem in various industries such as electronics, machinery, automotive, aerospace, oil, gas, and chemical engineering [1-2], since they were discovered by Brenner and Riddell [3]. The EN plating process makes possible to coat the insulators, conductors, internal surfaces of pipes, and the very difficult or even impossible surfaces to coat by conventional techniques.
In general, two reactions of alternating anodic/cathodic polarity on the surface of the substrate are responsible for the electroless of nickel and phosphorus; these reactions are given in equation (1) and (2):

\[
Ni^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Ni + 2H_2PO_3^- + H_2 + 2H^+ \tag{1}
\]

\[
2H_2PO_2^- + H^+ \rightarrow H_2PO_3^- + P + H + H_2O \tag{2}
\]

The composition, the crystal structure and the properties of electroless Ni-P alloys depends upon the deposition rate of the two competing reactions, which are controlled by the conditions and chemical composition of the bath solution. The Ni-P coatings are classified into three types versus the phosphorus content, low (1-3% P), medium (4-7% P) and high (7% P and more) phosphorus coatings [4-8]. In general, Ni-P with 1-6 % P is crystalline with high hardness, good wear and abrasion resistance. Conversely, when the phosphor exceeds 7 % or 8 % [1,9-11] the Ni-P coating is amorphous structure in nature and exhibit good corrosion resistance and solderability.

The additives present in EN bath like stabilizers, complexing and accelerators influence the deposition rate, morphology, structure and physical properties of the deposit [12-13]. The action of these different additives added to EN bath depends on several parameters such as their concentration, pH, temperature, solution fluid dynamics, and the reducing agents types [14]. Hence, it is evident that the right choice of stabilizers and accelerators for electroless nickel plating bath has to be made only after a careful study of the effect of these compounds on the plating rate and the coating characteristics.

Indeed, thiourea and lead acetate is commonly employed as stabilizers in electroless plating bath [15-16]. Complexing agents as sodium citrate, lactates, hydroxy-acetate, glycines, malonates and certain fluorites [17] can be added. The ammonium acetic is selected as the main complexing agent in the nickel electroless [18]. Also, CH$_3$COONa are added to the bath as the buffering agents [19]. Besides, the ammonium acetate was used as complexes-stabilizing agent in the baths of the Ni-P alloy [20-21] at basic medium and the Ni-Cu-P coating at acid medium [22]. However, our preview paper, we have justified the accelerator role of the ammonium acetate in the bath of electroless Ni-P in acid medium using sodium hypophosphite such as reducing agent [23]. The deposition rate, the surfaces morphology, the crystalline structure and the roughness of deposit depend on the ammonium acetate concentration. In the present work, the classic role of the ammonium acetate in litterateur is change to complexes-stabilizing agent to accelerator agent for the bath chemical of electroless Ni-P alloy. Thus, examine the effect of the acidity and composition of the formulation bath of
electroless Ni-P in the acidic medium with the new role of ammonium acetate an in-depth study is interested.

2. Experimental procedures

2.1. Preparation of the substrates

In this work, mild steel specimens of about 6 cm² of surface were prepared from rod stock to be used as substrates. The choice of the mild steel as basic substratum is dictated by for the reasons:

- The mild steel is the current metal a usage due to the reasonable price.
- Indeed, the mild steel is almost used everywhere: constructions, bridges, shipbuilding ferovière, automobile, engines and the machines.

Prior to immersion test, the substrate was abraded using emery paper up to 1200 grade, cleaned with acetone, etched in 10 % dilute sulphuric acid, washed with distilled water, and dried finally.

2.2. Plating bath and operating conditions

All solutions employed these experiments were freshly prepared from analytical grade reagents and distilled water. The composition of the plating bath for electroless Ni-P alloys is nickel sulfate as the source of nickel, sodium hypophosphite as the reducing agent, sodium citrate as complexing-stabilizer agent and ammonium acetate as the accelerator agent [23]. The specific bath compositions and plating conditions used are presented in Table 1.

<table>
<thead>
<tr>
<th>Component of the bath</th>
<th>Values</th>
</tr>
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<tbody>
<tr>
<td>NiSO₄·6H₂O / g L⁻¹</td>
<td>30</td>
</tr>
<tr>
<td>NaH₂PO₂·H₂O / g L⁻¹</td>
<td>23.5</td>
</tr>
<tr>
<td>Na₃C₆H₅O₇·2H₂O / g L⁻¹</td>
<td>10.5</td>
</tr>
<tr>
<td>CH₃COONH₄ / g L⁻¹</td>
<td>32.5</td>
</tr>
<tr>
<td>pH</td>
<td>5.5</td>
</tr>
<tr>
<td>T / °C</td>
<td>85(±1°C)</td>
</tr>
</tbody>
</table>

Indeed, the mixture of all the constituents of the bath gives an initial pH of the electrolyte close to 6. The pH of the bath was maintained between 4.5 and 7 by the addition of sufficient quantity of the acetic acid and/or by the ammonia water. The Temperature of the plating bath was maintained at 85°C (±1°C). The electrolyte temperature was controlled using a thermometer.
2.3. Analysis of deposits

The electrolysis cell was a borosilicate glass (Pyrex) cylinder closed by cap with five apertures. The deposition rate was estimated from weight gain after 1 h of immersion time, assuming a Ni coatings density of 8.9 g cm\(^{-3}\) [24]. The morphology was investigated by scanning electron microscopy, the composition estimated by EDX analysis and the crystalline structure by X-ray diffraction using a copper anticathode.

For the cyclic voltammetry measurements, a conventional three electrode cell was employed. It involved the use of glassy carbon samples as the working electrode, while the auxiliary electrode is a Pt plate. All potentials were measured and reported with respect to saturated calomel electrode (SCE). The polarization curve was recorded by polarization from 1200 mV/SCE towards more negative direction (-1200 mV/SCE) with a sweep rate of 10 mV/s which is the minimal value to observe the reaction occurred at the metallic surface. These measurements were carried out using Potentiostat/Galvanostat/Voltalab PGZ 100 monitored by a personal computer.

3. Results and discussion

The bath 1 with 32.5 g L\(^{-1}\) of the ammonium acetate used as accelerator, permit to elaborate a chemical deposit Ni-P alloys with a deposition rate of 18 µm h\(^{-1}\), and with a phosphor content of the order 6.4 % what confers a crystalline structure of this alloys [23]. The influence of technology parameter such as pH value, the concentrations of nickel sulphate, sodium hypophosphite, and sodium citrate, on the deposition rate, surface morphology, and structure of the Ni-P alloys was investigated. When studying the effect or the influence of one parameter of the bath 1 in the deposition rate or other properties, the other compositions of the bath were not changed.

3.1. Effect of electrolyte pH

The electrolyte pH was considered for a long time as the most important parameter for the deposition rate and composition of EN [25]. Various values were proposed according to the nature of the reducing agent used in the bath [26,27]. Fig. 1 shows the acidity effect on deposition rate and phosphorus content on the Ni-P alloy.
The examination of the results shows, the importance increase of the deposition rate from 6 to 18 µm h\(^{-1}\) with the increasing of the pH value from 4.5 to 7 in the plating bath 1, with a maximum of the plating rate between pH=5 and 5.5. Similar results were obtained in other study, when the rate of oxidation of the hypophosphite, on a nickel substrate, increases fourfold when the pH increases from 3 to 7 [25]. In addition, when the pH of the bath 1 is less than 5, a large possibility to decompose spontaneously of the bath was observed. This phenomenon can be justified by the accumulation of the H\(^+\) ions during the autocatalytic chemical reaction, which block the active sites of the substrate, consequently lower the deposition rate of the electroless process. Indeed, the increasing of the plating bath acidity causes the increase of the phosphorus content in the Ni-P alloys formed. This increase of the phosphor content is accompanied with a fall of the deposition rate at 5 µm h\(^{-1}\) which is followed by a big tendency to the decomposition of the bath. Similar results were found by other author [19]. On the other hand, when the pH value of the bath is superior to 5, the Ni-P alloy characterized with medium phosphor content and the deposition rate varies between 18 and 16 µm h\(^{-1}\).

Fig. 2 (a-d) shows the surface morphologies of Ni-P alloys elaborate at different values of pH in the bath 1.
For all coatings, a spherical nodular morphology of the Ni-P alloys can be observed. The nodules size and density increase with decreasing of the acidity of the bath 1. A relationship between the grains size and the phosphorus content in the Ni-P alloy is concluded. A similar result was indicated in the author work [28]. In addition, the deposits formed at pH = 4.5 (fig. 2(a)) is characterized by important number and diameter of porosity, which hindered the quality of the electroless Ni-P alloy despite the high phosphorus content in this case. However, when the pH of the bath is between 5 and 5.5, the electroless Ni-P alloy is more homogeneous and more compact (fig. 2(b) & (c)). This can be mainly attributed to the stability role of ammonium acetate, which can stabilize the nucleation and growth of grains.

The X-ray diffraction patterns of electroless Ni-P alloys obtained at different pH values of the plating bath are shown in Fig. 3.
Fig. 3: The X-ray diffraction patterns of electroless Ni-P alloys obtained using bath 1 at different pH values

It can be seen that the X-ray diffraction patterns of electroless Ni-P coatings exhibit only a single broad peak about $2\theta = 45^\circ$. When the acidity of the bath is less than or equal to 5, the Ni-P coating have an amorphous structure. While, when the acidity of the bath is greater than 5 the Ni-P alloy are crystalline nature. The XRD results confirm the results of EDX correspondent the phosphorus content in the Ni-P alloy (cf. fig. 1)

In conclusion, the acidity of the bath 1, in presence of 32.5 g L-1 of ammonium acetate as accelerator, affects the deposition rate, bath stability, quality of the deposit, phosphorus content consequently the structure of the Ni-P alloy developed in acid medium. The results of this party illustrates in general that the decreases of the acidity in the plating bath provoked the Ni-P alloy with a deposition rate and stability of the bath important and the Ni-P alloys characterized by a low phosphorus causes a crystalline structure dominant in this case.

3.1.1. Cyclic voltammetry studies

According to the mixed potential theory of electroless plating [29], the overall reactions usually result from two simultaneous reactions, i.e. the reduction of Ni$^{2+}$ ions and the oxidation of the reducing agent. However, several interactions often occur between these reactions [26,30]. For these, cyclic voltammetry was carried out to characterize the effect of
acidity of the bath on various red-ox processes. Fig. 4 shows the influence of the acidity bath, on the voltammograms of electroless Ni-P alloys using glassy carbon as working electrode.

**Fig. 4:** Voltammograms recorded on glassy carbon electrode of electroless Ni-P alloys at various pH values of the bath 1 (Scan rate / 10 mV s\(^{-1}\))

All voltammograms of electroless Ni-P alloys reveal the existence of:

A cathodic peak K representing to the reaction reduction of Ni\(^{2+}\), H\(_2\)PO\(_2^-\) and H\(_2\)O.

An anodic peak A located at 640 mV/SCE relating to the oxidation H\(_2\)PO\(_2^-\) ions and hydrogen atoms adsorbed at metallic surface.

Two peaks B (at 370 mV/SCE) and C (at 740 mV/SCE) represent the dissolution of the of Ni–P alloy in two stages, crystalline phase and amorphous phase respectively.

The currents densities evolution of anodic peak I\(_A\) corresponds at oxidation of hypophosphite versus acidity of the bath deposition is given in fig. 4. It is noted that the peaks intensities I\(_A\) increase with decreasing of the acidity of the bath indicating that this compound acts in anodic reaction of electroless nickel. This result confirmed the results obtained by gravimetric on the deposition rate (cf. Fig. 1).

3.2. **Effect of bath composition in electroless Ni-P alloys**

3.2.1. **Effect of the nickel ion source and reducing agent**

The nickel ion source and the reducing agent play a decisive role during the process of electroless nickel. The recent baths is characterized with the different concentration in sell metallic and in hypophosphite in terms of the composition and the condition of plating bath. In this party, we maintained the concentration constant of the components when in study the
effect of the authors constituent. The fig. 5, show the effect of the NiSO$_4$,6H$_2$O and NaH$_2$PO$_2$,H$_2$O concentration in the deposition rate of electroless Ni-P alloys.

![Deposition Rate vs Concentration](image)

**Fig. 5:** The deposition rate of electroless Ni-P versus the NiSO$_4$,6H$_2$O and NaH$_2$PO$_2$,H$_2$O concentration

It is noted, a similar effect of the nickel sulfate and the sodium hypophosphite concentration on the deposition rate of electroless Ni-P alloy in the bath 1. Indeed, the deposition rate of electroless Ni-P alloy of the two components presents an effect volcano with the increasing of this concentration. This effect volcano was also observed in other works during the elaboration of Co-P and Ni-B alloys [31-34]. In absence of the Ni$^{2+}$ or H$_2$PO$_2^-$ ions in the plating bath, we have absence of the autocatalytic reaction of deposit what is translated by deposition rate of deposit equal zero. This result express that the Ni$^{2+}$ and H$_2$PO$_2^-$ ions play a catalyst role of the autocatalytic chemical reaction of electroless Ni-P alloy. When the NiSO$_4$,6H$_2$O and NaH$_2$PO$_2$,H$_2$O concentrations increase at 30 and 23.5g L$^{-1}$ respectively in the bath 1, the rate deposition of Ni-P coating increase to get a maximum at 18 µm h$^{-1}$. This result can be explained by the increase reduced of the Ni$^{2+}_{\text{free}}$ ions escape to the complexes agent in the bath [35]. Comparable results were observed by other authors [31-33]. That is why there conclude a maximum dependence of the deposition rate with the concentration of the nickel ion source and reducing agent. However, when the NiSO$_4$,6H$_2$O or NaH$_2$PO$_2$,H$_2$O concentration is superior to 30 and 23.5 g L$^{-1}$ in the plating bath 1, an increase of the deposition rate of the Ni-P deposit is expected, but the Fig. 6 shows a decrease of the deposition rate. To explain this paradoxical action in electroless Ni-P deposit, we often resort
to the report molar $[\text{Ni}^{2+}] / [\text{H}_2\text{PO}_2^-]$]. When the concentration of the reducer agent is constant, and the concentration of the $\text{Ni}^{2+}$ ions is important in the bath 1, or the opposite case, the report $[\text{Ni}^{2+}] / [\text{H}_2\text{PO}_2^-]$ is destabilized, consequently a decomposition spontaneous of the bath 1 is observed. This decomposition can be explained, during the process of electroless nickel, by the oxidation of the largest part of the $\text{H}_2\text{PO}_2^-$ ions, escapes to the autocatalytique reaction of electroless Ni-P, in phospite ($\text{H}_2\text{PO}_3^-$) form. The progressive accumulation of the latter ($\text{H}_2\text{PO}_3^-$) ions provokes the decomposition of the bath accompanied with intense hydrogen evolution in the bath and massive precipitation of nickel germs and the electrolyte is characterized by a blackish coloring. In this work, the report molar $[\text{Ni}^{2+}] / [\text{H}_2\text{PO}_2^-]$ between these two constituents, for the maximum deposition rate of electroless Ni-P deposit ($18 \, \mu\text{m h}^{-1}$) and stability of the bath 1 is the order 0.52. This result is in agreement with Gutzeit and Krieg [36]. In other works, the report molar $[\text{Ni}^{2+}] / [\text{H}_2\text{PO}_2^-]$ to have a maximal rate deposition and acceptable stability vary between 0.3-0.4 [37-38] with other additives in the presence of the citrate trisodique.

3.2.3. Effect of complexant agent

The complexant agent plays an important role during the process of electroless Ni-P deposit, it is a chemical agent, added to the bath to slow down or prevent the initiating of the chemical reactions which activate the spontaneous decomposition of the bath. The Fig. 6, illustrate the effect of the $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot2\text{H}_2\text{O}$ concentration as complexant agent of the bath 1 on the deposition rate and the P content in the Ni-P alloys.

![Fig. 6: Dependence of the deposition rate and the P content in Ni-P coating on the sodium citrate concentration.](image-url)
In absence of the trisodium citrate, we observed a strong activity of the bath 1 accompanied with an intense emission of dihydrogen provoked a spontaneous decomposition of the bath in the first 10 min of the electroless processes. In this case, all of the Ni$^{2+}$ ions in the bath are free, by consequence these ions precipitate with other chemicals species existing in the electrolyte to give unstable bath. The electroless reaction of deposit is no more autocatalytic, but becomes a homogeneous chemical reaction and the Ni-P alloy is not more adherent, characterized with an aspect blackish. Nevertheless, the increase of the trisodium citrate concentration in the bath causes a decrease of the deposition rate which falls at 6 µm h$^{-1}$ when the Na$_3$C$_6$H$_5$O$_7$.2H$_2$O concentration is 40 g L$^{-1}$, accompanied with increase of the stability of the bath. At higher concentrations of trisodium citrate, the stability of the bath 1 are memorable but we attend the inhibition of the process of deposit because all of the Ni$^{2+}$ ions are had complexes. In conclusion, the addition of the trisodium citrate in the electroless bath, control the process of electroless Ni-P coating, by the decrease of the Ni$^{2+}$ free ions concentration in the bath. Similar results was Investigated in other works [39-40]. Besides, the addition of the trisodium citrate with various concentrations in the bath 1 influences also the phosphorus content in the Ni-P alloys. According the Fig. 6, we notice the increase of the P content in Ni-P alloys form 6.5 at 10 % with the increase of the trisodium citrate concentration from 10.5 to 30 g L$^{-1}$ in the bath.

The diffractogrammes DRX of the various Ni-P alloys prepared with the different concentation of the complexant is presented in the Fig 7.

Globally, it can be seen a single peak in $2\theta = 44^\circ$ representing the reflexion from the plane (111) with a change of the width and the intensity of the peak Ni(111) according to the Na$_3$C$_6$H$_5$O$_7$.2H$_2$O concentration in the bath. The DRX of the Ni-P alloys elaborate in low concentrations of trisodium citrate in the bath (Fig. 7 (A & B)) was characterized with intensity important and a very thin peak Ni(111). These results sign an important degree of crystallinity of the Ni-P alloys. However, the DRX of Ni-P prepared with important concentrations of trisodium citrate in the bath (Fig. 7 (C)), an important width is noted of the peak Ni(111). The deposit Ni-P obtained in these concentrations is characterized by a amorphous structure.
Fig. 7: XRD patterns of Ni-P alloys prepared with different concentration of trisodium citrate in bath 1

The surface morphology of Ni-P alloys prepared at different concentrations of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O in the bath 1 was indicated in Fig. 8.

According the Fig. 8, the morphology of the Ni-P coatings depends strongly with the concentration of the trisodium citrate in the bath 1. Indeed, more the concentration of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O increases, more the size of the agglomerates formed is important. When the trisodium citrate concentration is 10.5 g L$^{-1}$, the Ni-P alloys are characterized by uniform and rough surface compound of spherical particles with low size grading (Fig. 8 A). However, when the concentration of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O is double in the bath, we notice the appearance of the shape cauliflower (nodules with a different diameter) in the Ni-P alloys (Fig. 8 B). When the concentration of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O is important (30 g L$^{-1}$), the Ni-P coating present a smooth and compact surface with a low distribution of the nodule and the black spots color (Fig. 8 C). These spots represent the sites of the basic metal not covered by the Ni-P alloys; let be a porosity of the alloys.
Conclusion

The effect of the acidity and the composition of the bath on the deposition rate, the stability of the bath, the composition, the morphology, and the structure of the Ni-P coatings deposits are shown well for the bath 1 of electroless Ni-P alloys deposits in the presence of the ammonium acetate as accelerator agent of the bath. These results led us to fix the values of the pH and the components concentrations of the bath where the deposition rate and the stability of the bath are maximal. These values are 5.5 for the pH and the initial concentrations of the bath. In additions, we conclude:

1- For the electroless Ni–P alloys deposits, the deposition rates increase, approach a maximum value, and then decrease with the increase in the concentration of nickel...
sulphate, sodium hypophosphite and pH value. However, the deposition rates only decrease with increase in the sodium citrate.

2- The content of phosphorus in Ni-P alloys decreases from 10 to 6.4 % when the acidity of the bath increases from 4 to pH 6. However, the content of P increases from 6.5 to 10 % when the concentration of the sodium citrate increases in the bath from 10.5 to 30 g L⁻¹.

3- The surface morphology of the Ni-P alloys deposit depends on the acidity and the concentration of the complexant agent of the electroless bath. This surface morphology improved with the critical values of the acidity and the concentration of the sodium citrate.

4- The structure of the Ni-P alloys prepared with the plating bath 1 change to crystalline to amorphous structure with the P content in the coatings. The Ni-P alloys with the P content better than 7.6 % presented an amorphous structure. However, when the P content is less than 7.6 % the Ni-P coatings characterized by a crystalline structure.

5- The recorded voltammograms of the basic formulation show the general Chemical deposition diagram of the Ni-P alloy. This diagram is characterized by: A cathodic peak K relative to the reduction of the Ni²⁺, H₂PO₄⁻ ions and the H⁺. Three anodic peaks corresponding to the oxidation of certain compounds or to the dissolution of the alloys deposit phases. Indeed, the currents densities of anodic peak IA corresponds at oxidation of hypophosphite increase versus the acidity of the bath 1 provoked an increase of the rate deposition.

References