The Electroless Plating Ni-Fe-P Alloy and Its Voltammetric Behavior

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Abstract: Electroless Ni-Fe-P alloy deposition from an alkaline bath, containing sodium hypophosphite as reducer, boric acid as buffer agent and sodium citrate as complexing agent, was investigated. To increase the plating rate and to inprove the bath stability, the deposition parameters were optimized. The effects of process parameters (pH, temperature and mole ratio of $[Fe^{2+}]/([Ni^{2+}]+[Fe^{2+}])$) on the plating rate and deposit composition were examined and it was found that the presence of ferrous sulfate in the bath has an inhibitory effect on the alloy deposition. As a consequence, the percentage of iron in the electroless Ni-Fe-P alloys never reaches high values which is lower 20.0 %. Using cyclic voltammetry the electrodeposition mechanism of Ni-Fe-P alloys was investigated. It was observed that the presence of ferrous sulfate in the bath decreases the deposition rate and the iron doesn t catalyst on the oxidation of hypophosphite. However, the increase in temperature or pH leads to improving the deposition rate.

Key words: Electroless deposition, Ni-Fe-P alloys, Cyclic voltammetry, Electrodepositon

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1   Introduction

Electroless nickel-iron alloy films are of interest as promising materials for computer storage[1] and undercoating of recording media[1,3].. In the nickel-iron solution, deposition generally

proceeds only in the alkaline region , because the driving force of the reducing agent is not suffi-cient in the acid region. This may produce a problem , that is metallic ions naturally from hydr-oxide precipitates in the alkaline solution. In order to prevent precipitation , several organic chemicals have been used as complexing agents. Various nickel-iron solution have been developed to obtain soft magnetic films. During nickel-iron deposition , control of iron content is difficut , as it gets altered even with slight changes in operation condition. Phosphorus content in deposit can bring about an amorphous structure which incidentally improve the properties of the coating. It is Ni-Fe-P films deposited from solutions containing hypophosphite as reducing agent , sodium potas-sium tartrate as the complexing agent[1,4]. However , the electrochemical voltammetric behavior study of electroless plating Ni-Fe-P alloys has still not been completely developed.

In the precent work the electroless deposition and the electrodeposition of Ni-Fe-P alloy from a alkaline bath , containing sodium hypophosphite as reducer , boric acid as buffer agent and sodi-um citrate as complexing agent were studied to investigate the effect of iron on both processes. In the electroless deposition the effect of experimental parameters(pH ,temperature and the mole ra-tio of $[Fe^{2+}]/[Ni^{2+}] + [Fe^{2+}]$) on the plating rate and on the composition of the alloys were studied. The technique condition of Ni-Fe-P alloy electroless plating was optimized so as to obtain high deposition rate and good stability of the bath. Electrochemical investigations on the Ni-Fe-P electrodeposition were performed by means of cyclic volammetry. By studing the mechanism of Ni-Fe-P alloy electrodeposition , we can realized the mechanism of the electroless deposition , espe-cially the effects of the ferrous ion in bath.

2   Experimental details

Ni-Fe-P alloys were electrolessly deposited using a bath of the following composition : $NiSO_4$ · $6H_2O$ 10 18 g/ dm^3 , $FeSO_4$· $7H_2O$ 2 10 g/ dm^3 , NaH_2PO_2· H_2O 20 g/ dm^3 , $C_6H_5O_7Na_3$ 60 g/ dm^3 , H_3BO_3 30 g/ dm^3. The total concentration of $NiSO_4$· $6H_2O$ and $FeSO_4$· $7H_2O$ is 20 g/ dm^3. The temperate 50 95   and the pH was adjusted to 7. 0 9. 0 by the addition of sodium hydroxide. The solution was prepared with doubly distilled water and analytical grade reagents. This bath was chosen after some preliminary investigations on the chemical stability in order to avoid precipitation or spontaneous decomposition of the solution and to optimize the plating rate. The effect of temperature(from 50 to 95   ) , the pH(from 7. 0 to 9. 0) and the mole ratio of Fe-SO_4/ ($NiSO_4$ + $FeSO_4$) (from 0. 095 to 0. 486) were considered. The deposits were obtained on the carbon steel sheets of 8cm^2 surface area. These were mechanically polished and chemically etched in dilute sulphuric acid before the experiments. The plating rate was calculated from sam-ple weight gains. The composition of deposits was determined by an energy-dispersive X-ray spec-tral analysis for elemental analysis(EDX) attached by SEM.

The cyclic voltammograms were obtained from the same baths used for electroless deposition by means of a CHI832 Electrochemical Analyzer , but the concentration in the bath was decreased

by 50 %. The experiments were carried out with different process parameters. The working electrode was vitreous carbon of 0. 5 cm^2 surface area. It was selected as a substrate because it has a wide domain of electroactivity. The auxiliary electrode was a large area platinum plate(4 cm^2) and the reference electrode was a saturated calomel eleetrode(SCE). The scan rate was l0 mV· s^{-1}.

3   Results and discussions

3.1   Effect of plating parameters

The effect of pH on plating rate and deposit composition is shown in Figure 1. The deposition rate increases with pH, but the solutions become unstable at higher pH, especially above pH 9.0, ferrous hydroxide will precipitate during the plating process. With increasing pH the percentage of iron in deposits increases and the percentage of nickel decreases, and the percentage of phosphorus decreases. The similar behavior was also observed in electroless Ni-Zn-P plating[5].

Most investigation on electroless deposition has been carried out in the presence of hypophosphite as a reducer, and have shown that hypophosphite oxidation is the dominant factor in the electroless process. In alkaline media, according to Pourbaix diagrams[6], the oxidation of hypophosphite is

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

The incorporation of phosphorus in the deposit results from the disproportionation of $H_2PO_2^-$:

$$3H_2PO_2^- = 2P_{ads} + HPO_3^{2-} + OH^- + 2H_2O \qquad (2)$$

When the pH value increases, according to reactions (1) and (2), the rate of hypophosphite oxidation also increases and so the plating rate is accelerated[7], but the amount of incorporated phosphorus is decreased. So, the iron content in the deposits increases from 6. 33 % to 11. 91 % and adversely the phosphorus content in the deposits reduces from 21. 48 % to l7. 83 % when the pH value varied from 7. 0 to 9. 0(Figure l).

Figure 2 shows the effect of the metallic salt mole ratio [Fe^{2+}]/ ([Ni^{2+}] + [Fe^{2+}]) on the alloy deposition. It was found that the presence of iron in the electroless bath greatly affects the plating rate. Indeed, the rate is reduced monotonically as the metallic salt mole ratio rises. These results show that the ferrous sulfate in the bath reduces the deposition rate of electroless Ni-Fe-P alloys. In addition, the Figure 2 shows the iron and nickel contents in the deposit change in an opposite sense: that is on increasing the ferrous ions concentration in the bath, the nickel content decreases. the iron content in the deposits increases from 5. 13 % to 15. 62 % and reversely the nickel content in the deposits reduces from 75. 42 % to 65. 21 % when the metallic salt mole ratio [Fe^{2+}]/ ([Ni^{2+}] + [Fe^{2+}]) varied from 0. 095 to 0. 486(Figure 2). But the percentage of iron in the eleetroless Ni-Fe-P alloys never reaches high values.

The bath temperature is one of the most important factors affecting the rate of electroless alloy deposition; thus, the deposition rate was determined at temperature between 70 and 95
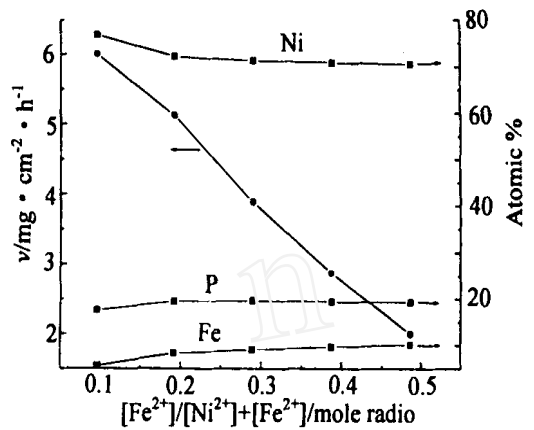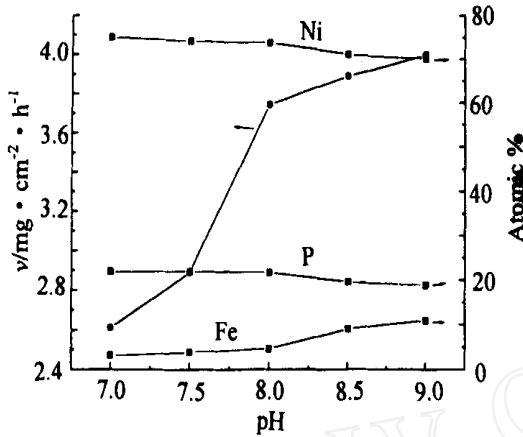
Fig. 1   Effect of pH on the deposition rate and on the percentage of Ni, Fe and P of the deposits
T: 90   ,   NiSO$_4$ · 6H$_2$O: 14   g/dm^3 ,
FeSO$_4$· 7H$_2$O :6 g/ dm^3

Fig. 2   Effect of metallic salt mole ratio [Fe^{2+}]/ ([Ni^{2+}]/ [Fe^{2+}]) on the depositionrate and on the percentage of Ni, Fe and P of the deposits
pH :8.5 , T :90

(pH 8.5). It was found that the deposition rate increases with increasing temperature (Figure 3).

3.2   Cyclic voltammetry

Voltammetric investigations were carried out at different condition to characterize the various oxido-reduction processes and investigate the effect of iron on the Ni-Fe-P alloy electrodepositiom.

Figure 4 shows the cyclic voltammograms obtained on vitreous carbon at l0 mV/ s. The deposition of the Ni-Fe-P alloy occurs at potentials more negative than about - 1.10 V (curve a), and three oxidation peaks in the deposition of the Ni-Fe-P alloy are observed (A$_1$, A$_2$ and A$_3$) in the anodic scan. In the absence of hypophosphite (curve c), only one anodic broad peak C are observed from - 0.80 to 0.50 V, related to the dissolution of Ni-Fe alloy. In the iron free solution (curve b), only two peaks (B$_1$ and B$_3$) are observed, these peaks were attributed respectively to the oxidation of hypophosphite and dissolution of Ni-P alloy[5]. Peak A$_1$ is not observed in the hypophosphite free solution and its intensity increases with the hypophosphite concentration in the bath (Figure 5). In figure 5, the hypophosphite concentration in the bath varied from curve a (0 mmol/ L) to curve d (113 mmol/ L). Thus, it is associated with the direct oxidation of hypophosphite, as already reported[5,8]. The reason is: in the case of electrochemical oxidation of hypophosphite reaction (1), the equilibrium potential of reaction(1), E_{eq}, is given by

$$E_{eq} = - 1.57 + \frac{3.4RT}{F}pOH + \frac{2.3RT}{2F}\log \frac{[H_2PO_3^-]}{[H_2PO_2^-]} \tag{3}$$

Where R is the gas constant, T is the temperature, and F is Faraday constant.. The value

of E_{eq} decrease with the hypophosphite concentration in the bath. So the intensity of peak A_1 increases. Peaks A_2 and A_3 are observed in the complete solution , these peaks were attributed respectively to the dissolution of Ni- Fe alloy and Ni- P alloy. The increase in peak A_3 with hypophosphite concentration (Figure 5) is due to the increase in phosphorous content in the film and confirms that this peak is associated with the dissolution of Ni- P alloy.
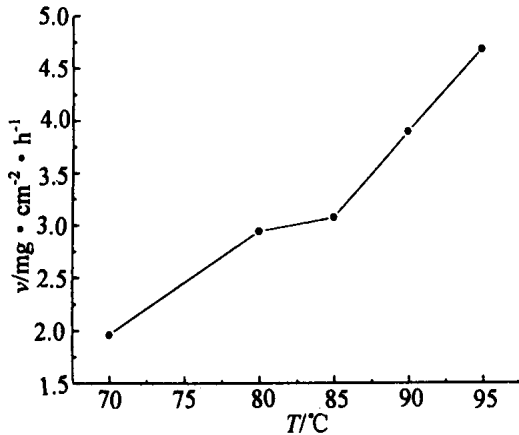

Fig. 3 Effect of temperature on deposition rate
$NiSO_4 \cdot 6H_2O : 14 \text{ g/ dm}^3$, $FeSO_4 \cdot 7H_2O :$
6 g/ dm^3 ; pH:8.5
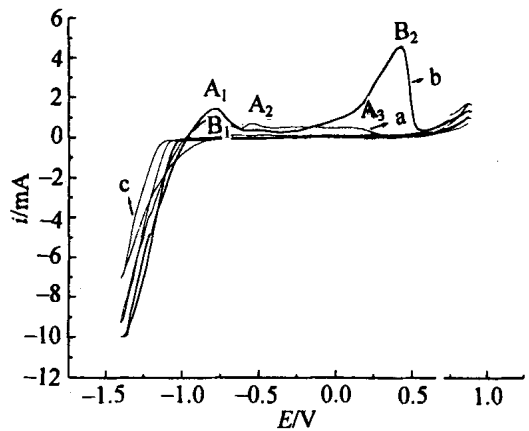
Fig. 4 Cyclic voltammograms obtained on vitreous carbon electrode
T:90 , pH: 8.5 , l0 mV/ s
a) Bath containing [Ni^{2+}] 26.6 mmol/L , [Fe^{2+}] 10.8 mmol/L and [$H_2PO_2^-$] 95 mmol/L , b) bath without Fe^{2+} , c) bath without $H_2PO_2^-$

Figure 6 shows the voltammograms obtained for various mole ratio of [Fe^{2+}]/ ([Ni^{2+}] + [Fe^{2+}]). The deposition current at the cathodic value of - 1.25 V decreases and the innition depositing potential shifts towards negative potentials(less noble potential) with increasing mole ratio of [Fe^{2+}]/ ([Ni^{2+}] + [Fe^{2+}]). This indicates that ferrous sulfate in solution reduces the deposition rate. According to the mixing potential theory , the deposition potential of Ni- Fe- P alloy E_m decreases with the mole ratio of [Fe^{2+}]/ ([Ni^{2+}] + [Fe^{2+}]). The intensities of peak A_3 decreases with increasing mole radio of [Fe^{2+}]/ ([Ni^{2+}] + [Fe^{2+}]) and also decreases with the phosphorous content in the film which varies from 21.75 % to 19.17 % ; this confirms that it is related to the dissolution of amorphous Ni- P alloy rich in phosphorous. The intensities of anodic peak A_1 of the Ni- Fe- P alloy is lower than that of the Ni- P alloy , and is almost not related to the amount of ferrous sulfate in the bath. The peak A_2 is associated with the oxidation of iron- nickel alloy from the deposit[5].
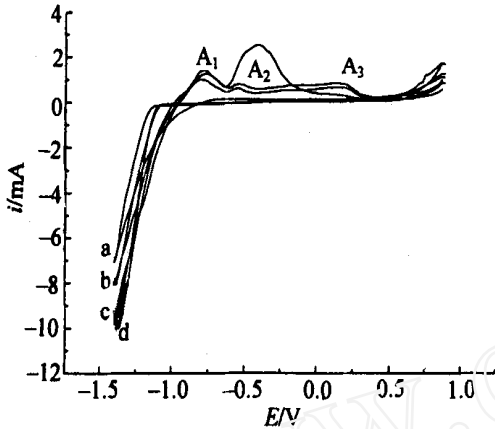
Fig. 5   Cyclic voltammograms obtained at various hypophosphite concentration

$[Ni^{2+}]$:26. 6 mmol/ L , $[Fe^{2+}]$:10. 8 mmol/ L , pH:8. 5 , T:90   , 10 mV/ s

a) $[H_2PO_2^-]$ 0 mmol/ L , b) $[H_2PO_2^-]$ 85 mmol/ L , c) $[H_2PO_2^-]$ 94 mmol/ L , d) $[H_2PO_2^-]$ 113 mmol/ L
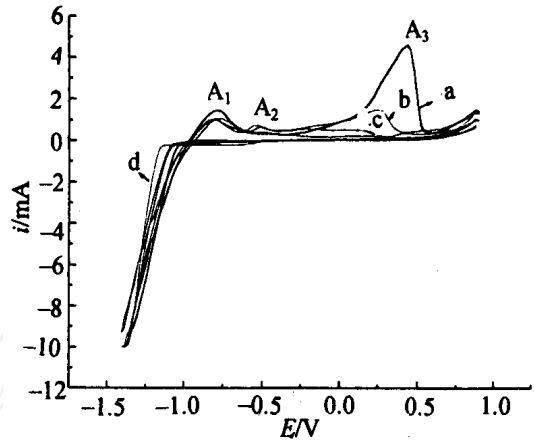
Fig. 6   Cyclic voltammograms obtained at various mole ratio of $[Fe^{2+}]/([Ni^{2+}]+[Fe^{2+}])$

$[H_2PO_2^-]$:94 mmol/ L , T:90   ;10 mV/ s

mole ratio $[Fe^{2+}]/[([Ni^{2+}]+[Fe^{2+}])$:

a) 0 ,b) 0. 192 , c) 0. 289 , d) 0. 486

It was found that the deposition potentials in the complete solution (curve b , c and d) and in the iron free soiution (curve a) are about - 1. 10 V and - 1. 05 V respectively ; and the deposition current at the cathodic limit of - 1. 25 V are about - 0. 004 A and - 0. 006 A respectively. These indicate that the electrodeposition rate of Ni- Fe- P is smaller than that of Ni- P. Because the deposition potential of iron in alkaline is more negative than that of nickel ; according to the mixing potential theory , the deposition potential of Ni- Fe- P is more negative than that of Ni- P.

Figure 7 shows the effect of the inversion potential in the range from - 1. 10 (curve a) to - 1. 25 V (curve d) . The cathodic current value and the intensities of anodic peak A_1 ,A_2 and A_3 increase with the inversion potential value. The increase of peak A_1 is associated with the increase in hypophosphite oxidation ,enhanced by the higher nickel content of the electrodeposits. The increase of peak A_3 indicates a greater electroreduction of nickel and hypophosphite. The increase of peak A_2 is indicates a greater electroreduction of iron- nickel. The total anodic peak A_2 and A_3 area is more than the cathodic peak area at each inversion potertial value ; this indicates the current efficiency is above 100 % due to an appreciable contribution of the electroless process. The parallel occurrence of the electroless process in the electrodeposition of Ni- Zn- P alloys was observed by Bouanani[5] and Swathirajan[9] at high temperature and at different current densities.

The effect of temperature is shown in Figure 8. The temperature increased from 50   (curve

a) to 90 (curve d). The deposition current at the cathodic limit - 1.4 V increases accompanied by a shift of 0.1 V in the deposition potential towards more positive value with temperature, due to the increase in deposition rate. The anodic peaks A_1, A_2 and A_3 all shift towards a more positive potential with temperature. This shows a high hypophosphite oxidation and Ni-Fe-P deposition rate increase in temperature enhances the nickel discharge[5].
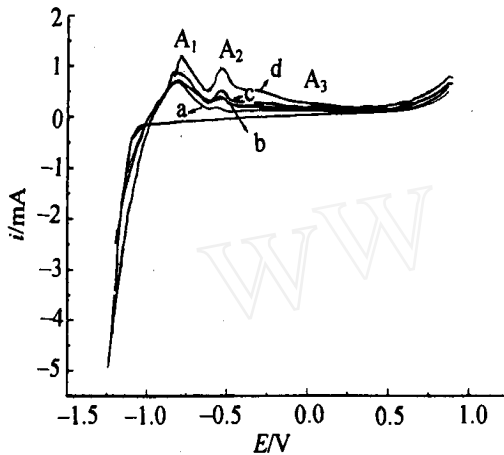

Fig.7 Cyclic voltammograms obtained at various inversion potential values
[$H_2PO_2^-$]: 94 mmol/L, [Ni^{2+}]: 26.6 mmol/L, [Fe^{2+}]:10.8 mmol/L, T:90 , pH:8.5, 10 mV/s
a) - 1.10 V, b) - 1.15 V, c) - 1.20 V, d) - 1.25 V

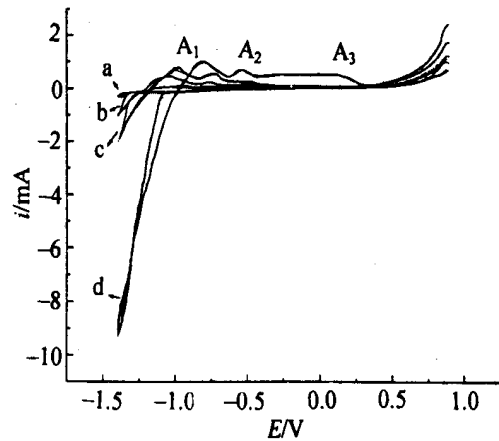Fig.8 Cyclic voltammograms obtained at various temperature
pH:8.5, 10 mV/s, [$H_2PO_2^-$]:94 mmol/L, [Ni^{2+}]:26.6 mmol/L, [Fe^{2+}]:10.8 mmol/L
a) 50 , b) 70 , c) 80 , d) 90

The effect of solution pH was examined (Figure 9). The deposition current at the cathodic limit of - 1.4 V increases with pH(curve a, b, c and d). this indicates the deposition rate increases with pH. The peak A_1 is enhanced when the pH becomes alkaline, this shows that the pH increase promotes hypophosphite oxidation. The reason is: in the case of equation (3), E_{eq} of the pH9 is more negetive than that of pH7. The decrease in peak A_3 with increase pH from 7 to 9 is related to the decrease in the phosphorous content in the alloy which varies from 21.48 % to 17.83 %.

4 Conclusions

From studies of plating rates and deposit composition in the electroless Ni-Fe-P alloy deposition from alkaline bath in the presence of hypophosphite as reducing agent. The flowing conclusion can be drawn:

1) The pH in bath affects on the deposition rate and on the composition of deposits. Increase in bath alkalinety favours the codeposition of iron, while the content of phosphorous in the alloy decreases with it.

2) The deposition rate decrease with the mole ratio of $[Fe^{2+}]/[Fe^{2+}]+[Ni^{2+}]$, but the percentage of iron increases with it and the percentage of nickel decreases with it. The precence of iron in the bath has in inhibitory effect on the alloy deposition, leading to low plating rates. As a consequence, the pencentage of iron in the alloy can never reach high values.

3) The temperature affects greatly on the deposition rate.

Fig. 9   Cyclic voltammograms obtained at various pH value

T:90   , 10 mV/s, $[H_2PO_2^-]$: 94 mmol/L, $[Ni^{2+}]$:26.6 mmol/L, $[Fe^{2+}]$:10.8 mmol/L

a) pH 7.0, b) pH 8.0, c) pH 8.5, d) pH 9.0

Cyclic voltammetry, carried out with the same baths for electroless deposition but the concentration in the bath was decreased by 50%, leads to the following results:

1) Increase in temperature favours the electrodeposition of Ni-Fe-P.

2) The pH favours the oxidation of hypophophite and increases the content of iron in the deposits. But content of phosphorous in the alloy decrease will it.

3) Iron deposites preferentially with inhibition of nickel discharge, and consequently, with depletion of nickel catalytic activity on hypophosphite oxidation.
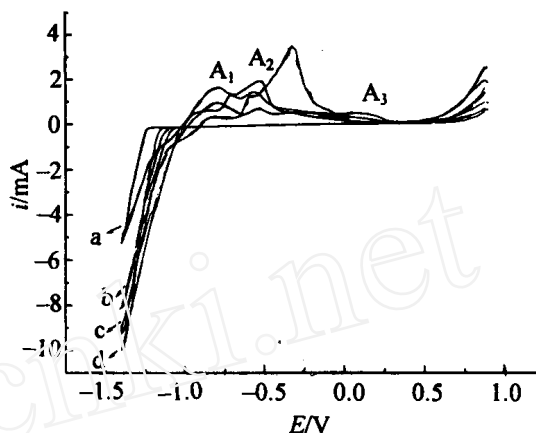
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-       (pH   , $[Fe^{2+}]/([Ni^{2+}] + [Fe^{2+}])$)

;   .   ,   - -

(   ) ,   (20 %) ,

- -   .   ,

pH   .

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