Effects of Complexing Agents on the Corrosion Resistance of Electroless Ni- Fe-P Alloys

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Electroless Ni–Fe–P alloys were deposited onto copper substrate from a bath using tri-ammonium citrate and/or tri-sodium citrate as complexing agents. The effects of complexing agents on the corrosion resistance of the alloys were investigated. The variation of the complexing agent leads to the change of corrosion resistance of the alloys due to the composition and the structure change, the alloys obtained with tri-ammonium citrate as complexing agents show better corrosion resistance than those with tri-sodium citrate as complexing agents. The alloys have better corrosion resistance in alkaline solution than in acid solution due to the increasing of polarization resistance.

1. INTRODUCTION

In the field of magnetic data storage devices, thin film magnetic heads have played an important role in enhancement of the magnetic recording density. Nickel-iron alloys have desirable soft magnetic properties and low coefficients of thermal expansion, making commercial alloys such as permalloy and invar an important component of magnetic storage devices or bimetallic temperature sensors, respectively [1-5]. The addition of a small amount of P or B improves the synthetic magnetic properties of permalloy films by increasing the resistivity value (ρ) [6–8]. Moreover, the presence of P or B in Fe-Ni film can bring about an amorphous structure, which improves the ductility, corrosion resistance properties[9,10].

Compared with other methods to prepare Fe, Ni films, electroless deposition can be used to produce uniformly thick, hard and corrosion-resistant films on various material substrates with different shapes[3,5,6,11-15]. Previous studies have reported the effects, such as pH and mole ratios of $FeSO_4/(NiSO_4+FeSO_4)$ in the bath, on the deposition rate, composition, structure and microhardness of Ni-Fe-P electroless alloys[5,12,16]. It is known that complexing agents are usually added in the bath to form complexes with metal ions to insure the plating bath stability, reasonable metal deposition rate and acceptable quality of alloys. Although the effects of complexing agents on the electroless Ni-P alloy and copper deposition have been investigated extensively [17-20], there is few investigation on the effects of complexing agents on the electroless Ni-Fe-P alloys.

In this work, we focus on the effects of complexing agents on the corrosion resistance of electroless Ni-Fe-P alloys from alkaline solutions. XRD, SEM, gravimetric and electrochemical measurements were employed to characterize the Ni-Fe-P alloys.

2. EXPERIMENTAL

Ni–Fe–P alloys were electrolessly deposited by using a sulphate bath with the composition listed in table 1. The total concentration of tri-ammonium citrate and tri-sodium citrate was fixed at 165 mM. The alloys were prepared on the copper substrates, which were pretreated prior to deposition. The deposition time was one hour. The alloy thickness was determined by measuring the weigh increment before and after deposition by electronic microbalance model HT-300. The composition of the alloys was examined using scanning electron microscopy (SEM, JEOL JSM—6700) combined with energy dispersive spectrometry (EDS). The structure of the alloys was analyzed by XRD (Siemens 5000).

Table 1. Chemical compositions of electroless Ni-Fe-P plating bath

reagent	Concentration, mM
$(NH_4)_3C_6H_5O_7$	0-165
$(Na)_3C_6H_5O_7.2H_2O$	0-165
$FeSO_4 \cdot 7H_2O$	54
$NiSO_4 \cdot 6H_2O$	29
$NaH_2PO_2 \cdot H_2O$	311
$C_{12}H_{12}O_{11}$	6
$NH_3.H_2O$	25 mL/L

Corrosion resistance in 1 M HCl and 1M NaOH solution at room temperature were determined by measuring weight loss. The weight of alloy was calculated by weighing the samples before and after corrosion by electronic microbalance. The average corrosion rate was determined by dividing the alloy weight by the surface area of substrate and corrosion time.

The corrosion resistance of Ni-Fe-P alloys was also investigated by electrochemical measurement. Potentiodynamic polarization measurements were performed using an autolab CHI-

660B galvanostat/potentiostat system. The measurements were performed using a conventional three-electrode cell. The working electrode was the copper electrode (φ = 19 mm) embedded in an epoxy resin, which was coated with Ni-Fe-P alloys in bath for one hour. A platinum foil with size 20mm × 40mm serves as an auxiliary electrode and a saturated calomel electrode was used as reference electrode. Prior to the beginning of the polarization measurements the sample was immersed in the corrosive medium (1M HCl or 1M NaOH) for about 10 min in order to establish the steady state potential. The sweep rate was 1 mV/s. The corrosion potential (E_{corr}), the corrosion current density (i_{corr}) and polarization resistance (R_p) were deduced from the Tafel plot (that is, log i versus E plot). The corrosion current is obtained using the Stern–Geary equation:

$$I_{corr} = \frac{b_a b_c}{2.303 R_p (b_a + b_c)}$$

where b_a and b_c are the Tafel slopes or the Tafel constants, and R_p the polarization resistance. The polarization resistance R_p is calculated using the following equation:

$$R_P = (\frac{\Delta E}{\Delta i})_{E \to Ecorr}$$

3. RESULTS AND DISCUSSION

The composition of the electroless deposited Ni-Fe-P alloys determined by EDS is shown in Table 2. The alloys consist of Ni about 69 atom %, P ranging from 22.80 to 26.20 atom %, and Fe in the range of 4.83-8.24 atom %, respectively. With the increase of the ratio of [NHCit]/[NaCit+NHCit] in bath, nickel content in the alloy changes little, phosphorus content increases, while iron content decreases.

Table 2. Chemical compositions of electroless Fe-Ni-P alloys

[NaCit]/[NaCit+NHCit]		1	0.5	0
Component Content (atom %)	P	22.80	24.29	26.20
	Fe	8.24	5.91	4.83
	Ni	68.96	69.80	68.97

The XRD technique, which provides information on the property of the alloys, has been considered as one of the tools to investigate their chemical behavior. The XRD patterns of Ni-Fe-P alloys are shown in Fig.1. All the alloys show typical amorphous diffraction patterns with broaden

peaks. The full width at half maximum of these peaks increase with the ratio of [NHCit]/[NaCit+NHCit] increase, which corresponds to the increase of phosphorus content.

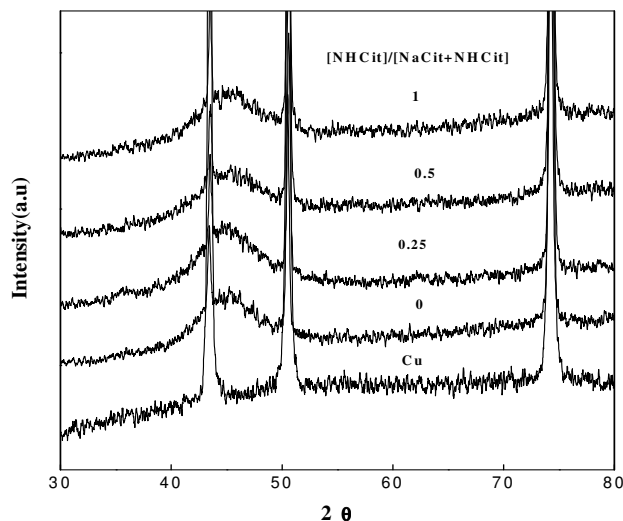**Figure 1.** The XRD patterns of Fe-Ni-P alloys deposited from the bath with different [NHCit]/[NaCit+NHCit] ratio

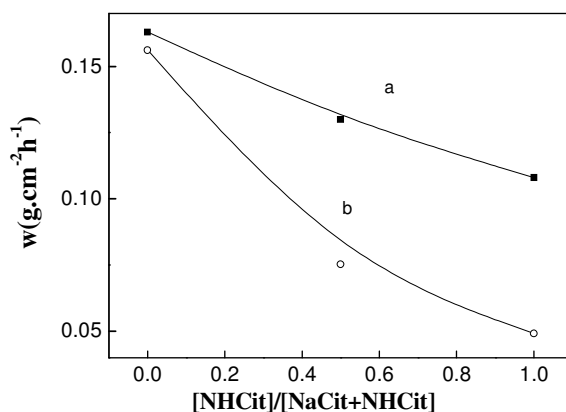**Figure 2.** The [NHCit]/[NaCit+NHCit] dependencies of corrosion rate of alloys in HCl solution (a) derived from weight loss measurement (b) derived from polarization measurement

The corrosion resistance of the as-plated electroless Ni-Fe-P alloys in 1 M HCl and 1M NaOH solutions was investigated by weight loss tests and electrochemical technique. The effect of complexing agents on the corrosion rate of alloys in 1 M HCl was displayed in Fig.2. It can be seen clearly that the weight loss of the alloys decreases with the increasing of NHCit in bath. Potentiodynamic polarization measurement was also performed to reveal the dependence of corrosion resistance of alloys on the bath composition. Fig.3 shows the polarization curves for electroless Ni-Fe-

P alloys in 1 M HCl solution. The electrochemical corrosion parameters obtained from the Tafel polarization curves are listed in Table 3. Table 3 shows that the corrosion potential shifts positively, while the corrosion current of alloys decrease in 1 M HCl solution with the ratio of [NHCit]/[NaCit+NHCit] increase. The corrosion rate, w_2(mg/cm^2·h), can also be calculated from the corrosion current, i_{corr} (A/dm^2), using Faraday's law

$$w_2 = \frac{i_{dep}}{F}\frac{W}{n} = 0.373 N i_{dep} = 10.82 \times i_{dep} (mg \cdot cm^{-2} \cdot h^{-1})$$

where F is the Faraday constant, W the average atomic weight of alloy (supposing $W= 58$), n the number of electrons obtained by metal ion ($n = 2$), $N=W/2 = 29$. As shown in Fig.2, the corrosion rates derived from polarization curves show similar trend to that determined from weight method, i.e., the corrosion rate of alloy decreases with the increasing of NHCit.
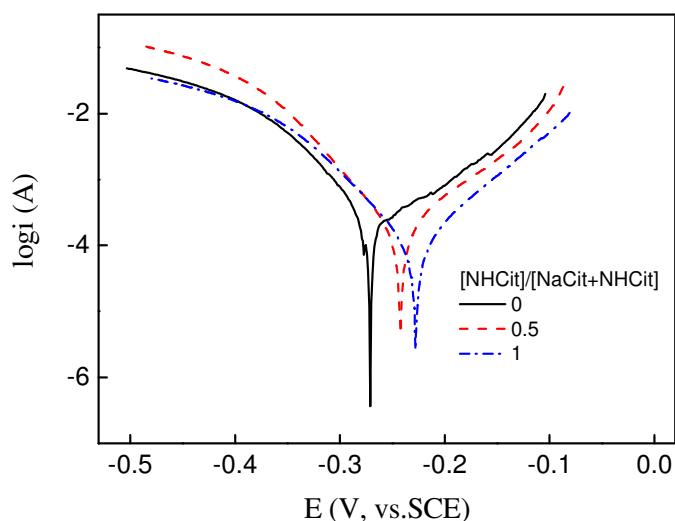

Figure 3. Potentiodynamic polarization curves of elelctroless Ni-Fe-P alloys in 1M HCl solution

Table 3. Corrosion characteristics of the electroless Ni-Fe-P alloys in 1 M HCl solution

[NHCit]/[NaCit+NHCit]	0	0.5	1
E_{corr}(V)	-0.27	-0.24	-0.23
b_c	9.351	13.93	11.89
b_a	12.48	14.26	13.35
R_p	48.69	78.22	133.9
$I(\mu A)$	409	197.2	128.7

Fig.4 displays the alloy thickness dependence on immersion time for Ni-Fe-P alloys in 1M NaOH solution at room temperature. As shown in Fig.4, the alloy thickness for one-hour deposition decreases with the increasing of NHCit in bath. The thickness of alloy obtained in bath with NaCit as

complexing agent is about 1.5 times of that obtained in bath with NHCit as complexing agent, which shows that the deposition rate decreases with increasing the ratio of [NHCit]/[NaCit+NHCit] in the bath. However the alloy thickness decreases abruptly with the immersion time for the alloy obtained in bath with NaCit as complexing agent, while that decreases little for the alloy with NHCit as complexing agent, suggesting the alloy obtained with NHCit as complexing agent shows better corrosion resistance.
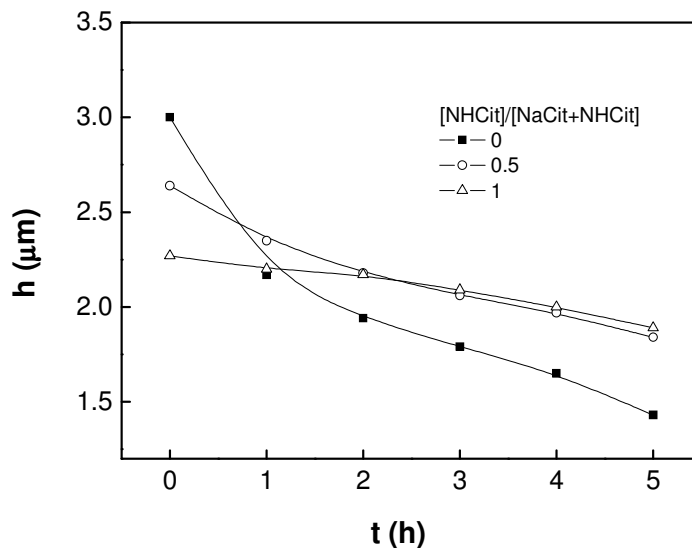

Figure 4. The alloy thickness dependence on immersion time for Ni-Fe-P alloys in 1 M NaOH solution at room temperature
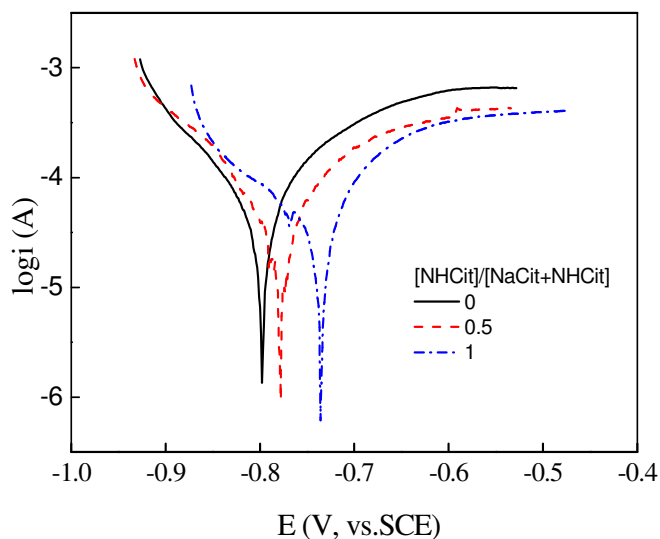

Figure 5. Potentiodynamic polarization curves of elelctroless Ni-Fe-P alloys in 1M NaOH solution

Fig.5 shows the polarization curves for electroless Ni-Fe-P alloys in 1 M NaOH solution and the electrochemical corrosion parameters obtained from the Tafel polarization curves are listed in Table 4. It can be concluded from Table 4 that the corrosion potential shifts positively, while the corrosion current of alloys decreases in 1 M NaOH solution with the ratio of [NHCit]/[NaCit+NHCit] increase. Compared with the electrochemical corrosion parameters of alloys in HCl solution, the polarization resistance is much greater while the corrosion current is much lower in NaOH media, indicating the alloys have better corrosion resistance in NaOH than in acid solution.

Table 4. Corrosion characteristics of the electroless Ni-Fe-P alloys in 1 M NaOH solution

[NHCit]/[NaCit+NHCit]	0	0.5	1
E_{corr}(V)	-0.80	-0.78	-0.74
b_c	11.17	7.961	9.998
b_a	4.481	3.522	3.279
R_p	368.8	415.2	468.7
$I(\mu A)$	75.31	72.254	69.87

As discussed above, the alloys obtained with NHCit as complexing agent show better corrosion resistance. This can be contributed to the increase of phosphorus content in the alloy. It is known that the corrosion resistance of any alloy depends largely on the ability to form a surface protective film. The EDS analysis shows that alloy obtained with NHCit as complexing agent has higher content of phosphorus, which can make the corrosion potential increase and the corrosion current decrease[14], Hence, the better corrosion resistance for electroless Ni–Fe-P alloy obtained with NHCit as complexing agent can be attributed to the phosphorous increase in the alloy, which facilitate to form amorphous structure and passivation film.

4. CONCLUSION

Ni–Fe–P electroless alloys were obtained from a bath using tri-ammonium citrate and/or tri-sodium citrate as complexing agents, the total concentration of which was about 165 mM. The deposition rate of alloy decreases with increasing the ratio of [NHCit]/[NaCit+NHCit] in the bath. While the corrosion resistance of alloy increases with the increasing of ratio of [NHCit]/[NaCit+NHCit] in the bath, corresponding to the decrease of iron content and increase of phosphorus in the alloy, which facilitates to form amorphous structure and passivation film, thus improves the corrosion resistance of alloy. The corrosion resistance of alloy in NaOH solution is much better than that in HCl solution.

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