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The Effect of Ferrous Sulphate on the Electroless Deposition of Co-Fe-P Alloys

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Abstract: Electroless deposition of Co-P alloy and Co-Fe-P alloy from an alkaline bath, containing sodium hypophosphite as a reducer, boric acid as a buffer agent and sodium citrate as a complexing agent, was investigated respectively. The effects of process parameters, such as pH of solution and metallic salt mole ratio of $CoSO_4$/ $FeSO_4$, on the plating rate were examined. It was found that the presence of ferrous sulfate in the bath has an inhibitory effect on the alloy deposition. As a consequence, the plating rate of Co-Fe-P is lower than that of Co-P. The electrochemical polarization measurements have been carried out to examine the effect of ferrous sulphate on the cathodic or the anodic polarization process. The ferrous sulphate affects both the cathodic and anodic polarization processes, which reduces the deposition current and potential. The results of the electrochemical polarization experiments agree well with those of electroless deposition rate measurements.

Key words: Electroless deposition, Alloys, Cobalt, Iron, Electrochemical polarization

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1 Introduction

The magnetic thin films are key materials for various functional devices such as high-density data storage systems. The soft magnetic films plated by electroless was studied, especially Ni-Co-P [1,2] and Co-P[3-5] alloys deposits. Because metal iron has good magnetic performance, Ni-Fe alloy and Co-Fe alloy are soft magnetic materials in order to achieve higher performance levels, which have been applied widely in the fabrication of magnetic memories for computer application. However electroless Co-Fe-P films has received less attention. We have studied electroless deposition Co-P, on this base we plated Co-Fe-P by add $FeSO_4$ in the electroless Co-P solution. In our previous work,

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we have studied the effect of deposition conditions on the composition , structure and microhardness of Co-Fe-P deposit.

In this study , an electroless Co-Fe-P solution was investigated. The relationship between the deposition conditions and the deposition rate was studied. Especially , the effect of ferrous sulphate in the solution on the deposition rate was studied by electrochemical polarization measurements.

2 Experimental Details

Co-Fe-P alloys were electrolessly deposited using a bath of the following composition: $CoSO_4·7H_2O$ 0.06~0.09 mol/L , $FeSO_4·7H_2O$ 0.04~0.01 mol/L (the total concentration of $CoSO_4·7H_2O$ and $FeSO_4·7H_2O$ is 0.1 mol/L) , $NaH_2PO_2·H_2O$ 0.2 mol/L , $C_6H_5O_7Na_3$ 0.3 mol/L , H_3BO_3 0.5 mol/L. The temperature of bath was kept at 90 ℃ and the pH was adjusted to 7.0~8.5 by solution of sodium hydroxide. The plating time was 2 h. Electroless Co-P alloys were plated at the same conditions , except the metallic salt $CoSO_4·7H_2O$ 0.1mol/L. The carbon steel sheet was used as substrate of which is 2 cm^2 in surface area. The substrates were mechanically polished and chemically etched in dilute sulphate acid before the experiments. The solution was prepared with distilled water and analytical grade reagents. The range of pH in the solution (from pH 7.0 to pH 8.5) and of mole ratio of $CoSO_4·7H_2O$ to $FeSO_4·7H_2O$ (from 0.09/0.01 to 0.06/0.04) were investigated respectively.

The deposition rate v ($mg·h^{-1}·cm^{-2}$) for plating of 2 h was calculated from sample weight gains.

The electrochemical polarization experiments were carried out in the same as "half electroless plating baths" by means of a CHI630A Electrochemical Analyzer with different process parameters. In order to simulate partial cathodic or anodic reaction , the investigation of the electrolytes in the absence of either the reducer (NaH_2PO_2) or the metallic salt (cobaltous sulphate and ferrous sulphate) was carried out. The polarization measurements were made in "half electroless plating baths" with various pH and various concentration of $FeSO_4$ (the concentration of $CoSO_4$ is always 0.1 mol/L) . The pH of solution was measured by electronic pH-meter. The mixed potential of electroless deposition was measured vs. SCE. The polarization curves were measured with the scan rate of 5 $mV·s^{-1}$ at temperature 70 ℃. All solutions were sparged with N_2 prior to and during the measurements. The working nickel electrode was round foil whose diameter is 0.6 cm. The auxiliary electrode was a large area platinum plate (3 cm^2) and the reference electrode was a SCE (saturated calomel electrode) . The potential of the working electrode was measured vs. SCE via the luggin capillary.

3 Results and Discussions

3.1 Deposition Rate

The effect of solution pH on the deposition rate of Co-P and Co-Fe-P alloys is illustrated in Fig. 1. Here the metallic salt mole ratio of $CoSO_4$/ $FeSO_4$ was 0.09/0.01 and 0.08/0.02 , respectively. Figure 1 shows that deposition proceeds with pH range from 7.0 to 8.5. Below pH 7.0 , deposition scarcely initiated and above pH 8.5 , the deposition rate was very slow. Both the Co-Fe-P and Co-P curves are found

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to have a peak around pH 7.7. The Co-P curve is above the two Co-Fe-P curves. This shows that the deposition rate Co-P is higher than that of Co-Fe-P. This behavior is not the same as those of electroless plating Ni-Zn-P[6] and Ni-Fe-P [7] deposits. Most investigation on electroless deposition has been carried out in the presence of hypophosphite as a reducer, and has shown that hypophosphite oxidation is the dominant factor in the electroless process. In alkaline media, the oxidation of hypophosphite is:

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

In the beginning when the pH value increases, according to above reaction, the rate of hypophosphite oxidation also increases and so the plating rate is accelerated. Afterward, especially above pH 7.7, cobaltous hydroxide and ferrous hydroxide will likely precipitate during the plating process, and these decrease the deposition rate.

Second, the effect of mole ratio of $CoSO_4$/ $FeSO_4$ on the deposition rate of Co-Fe-P alloy was investigated. The result is shown in Fig. 2. In this case the pH of solution was 7.7 and 8.0 respectively. The deposition rate decreased monotonically as the metallic salt mole ratio rises. When the mole ratio is 0.06/0.04, the deposition rate is very slow. This indicates that ferrous sulphate in the solution inhibits the electroless deposition of Co-Fe-P deposit.

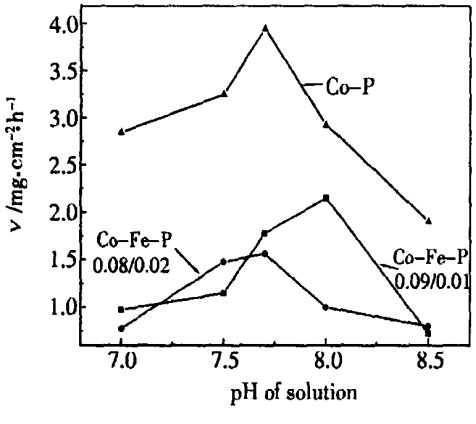

Fig. 1 Effect of solution pH on the electroless deposition rate of Co-P and Co-Fe-P alloys

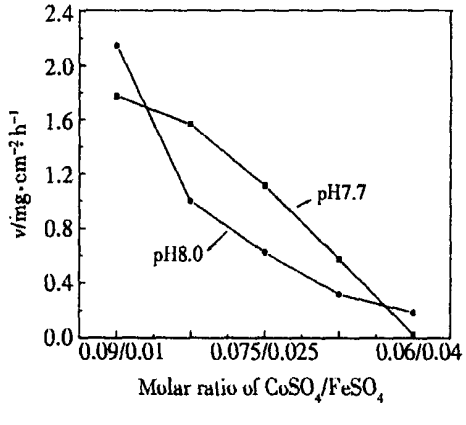

Fig. 2 Effect of molar ratio of $CoSO_4/FeSO_4$ on the electroless deposition rate of Co-Fe-P alloy

3.2 Electrochemical Polarization

Fig. 3 is the Tafel curves for the cathodic polarization and the anodic polarization (Evans diagram) of Co-Fe-P in eletrotyte of pH 7.0 and pH 8.5 respectively. Here, the cathodic polarization curves were made in the solution $CoSO_4$ 0.08 mol/L, $FeSO_4$ 0.02 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L and the anodic polarization curves were made in the solution which contains NaH_2PO_2 0.2 mol/L,

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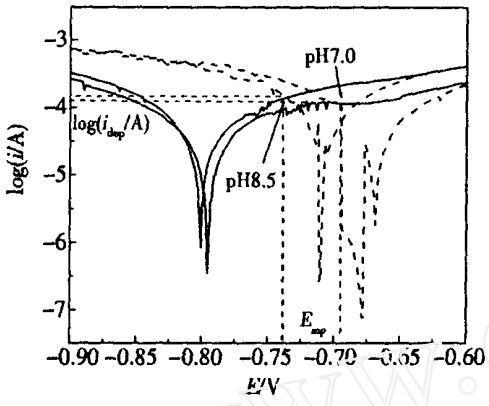

Figure 3　Tafel curves of the cathodic polarization and the anodic polarization (Evans diagram for Co-Fe-P in electrolyte of pH 7.0 and pH 8.5, respectively
cathodic solution: $CoSO_4$ 0.08 mol/L, $FeSO_4$ 0.02 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L
anodic solution: NaH_2PO_2 0.2 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L

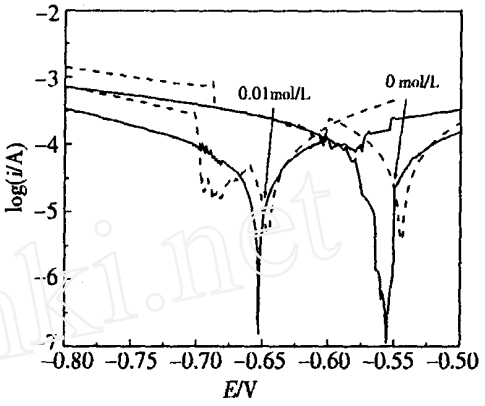

Fig. 4　Effect of $FeSO_4$ concentration on the Tafel curves for the cathodic polarization and the anodic polarization (Evans diagram)
cathodic solution: $CoSO_4$ 0.1 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L pH 8.0
anodic solution: NaH_2PO_2 0.2 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L pH 8.0

$C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L. The intersection of the anodic (solid line) and the cathodic (dash line) polarization curves represents, in terms of the mixed potential theory [8,9], the mixed potential E_{mp} (abscissa) and deposition rate i_{dep} (ordinate). According to Paunovic M. "Electrochemical aspects electroless deposition of metals" [9], "The rate determining process" in this process is the oxidation of hypophosphite reaction. The results of electrochemical study on Co-P in different pH of solution are basically the same as that of Co-Fe-P. In eletrochemical polarization of Co-P experiments, the cathodic polarization curves were made in the solution which contains $CoSO_4$ 0.1 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L and the anodic polarization curves were made in the solution which contains NaH_2PO_2 0.2 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L.

The effect of concentration of $FeSO_4$ on the Tafel curves for the cathodic polarization and the anodic polarization combined into one graph (Evans diagram) in solution pH 8.0 is shown in Fig. 4. Here, the cathodic polarization curves were made in the solution which contains $CoSO_4$ 0.1mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L and the anodic polarization curves were made in the solution which contains NaH_2PO_2 0.2 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L. The increase of $FeSO_4$ concentration causes a shift of the cathodic (dash line) and the anodic (solid line) polarization curves toward the negative potential. The cathodic and the anodic polarization currents decrease with the increase of $FeSO_4$ concentration. What factor causes the effect of $FeSO_4$ on the anodic polarization curves? This is prob-

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ably caused by the adsorption of $FeSO_4$ on the working electrode, which reduces the adsorption of hypophosphite, and so decreases oxidation of hypophosphite. Also we have found that "the rate determining process" is the oxidation of hypophosphite reaction without $FeSO_4$ in the solution, but when added 0.01mol/L $FeSO_4$, the process is under "the mixed determining process" (the mixed of the oxidation of hypophosphite reactions and the reduction of metallic salt ions reactions). The results of electrochemical polarization study are shown in Fig. 5.

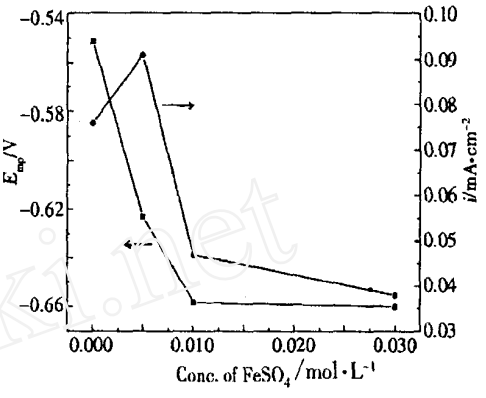

Fig. 5 Dependence of mixed potential and current density on the $FeSO_4$ concentration, components of cathodic/anodic solution same as in Fig. 4

Fig. 5 presents the dependence of mixed potential (E_{mp}) and deposition rate on the concentration of $FeSO_4$. It can be seen that both mixed potential (E_{mp}) shifts the nagative potential and current density (i_{dep}), i.e., deposition rate, decreases with the increase of concentration of $FeSO_4$, basically. On the whole, these results agree with the results of actual electroless Co-Fe-P plating rate measurements. In conclusion, ferrous sulphate affects both the cathodic and the anodic polarization processes, which lowers the deposition current and potential.

The dependence of mixed potential (E_{mp}) on pH of solution is shown in Fig. 6. The E_{mp} for Co-Fe-P or for Co-P is shifted cathodically with the increase of pH, basically. The reason is: in the case of electrochemical oxidation of hypophosphite reaction (1), the equilibrium potential of reaction (1), E_{eq}, is given by:

$$E_{eq} = -1.57 + 3.4RT/F \times pOH + 2.3RT/2F \times \log([HPO_3^{2-}]/[H_2PO_2^-]) \quad (2)$$

Where R is the gas constant, T is the temperature, and F is Faraday constant. When the pH of solution becomes alkaline, in the case of equation (2), E_{eq} becomes more negative. Also, the E_{MP} for Co-P is more positive potential than that of Co-Fe-P.

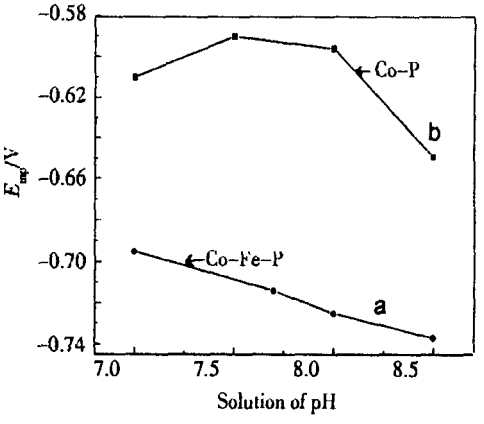

Fig. 6 Dependence of the mixed potential on the electrolyte pH
for Co-Fe-P (a) and Co-P (b), cathodic solution: (a) $CoSO_4$ 0.08 mol/L, $FeSO_4$ 0.02 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L, (b) $CoSO_4$ 0.1 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/Lanodic solution: a) NaH_2PO_2 0.2 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L, b) NaH_2PO_2 0.2 mol/L, $C_6H_5O_7Na_3$ 0.3 mol/L, H_3BO_3 0.5 mol/L

Fig. 7 shows the dependence of deposition rate on pH of solution. Current density, i.e., the deposition rate for Co-Fe-P or for Co-P increases when pH of solution ranges from 7.0 to 7.7 or to 7.5, then decreases with it. This also shows the deposition rate of Co-Fe-P is lower than that of

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Co-P. These results accord with that of actual electroless plating rate measurements.

4 Conclusions

From studies of plating rate in the electroless Co-P and Co-Fe-P alloys the following conclusions can be drawn:

1) In the beginning when the pH value increases, the plating rate is accelerated; but above pH 7.7, it decreases.

2) The presence of ferrous sulphate in the bath has an inhibitory effect on the alloy deposition, leading to low plating rate. As a consequence, the plating rate of Co-Fe-P is lower than that of Co-P.

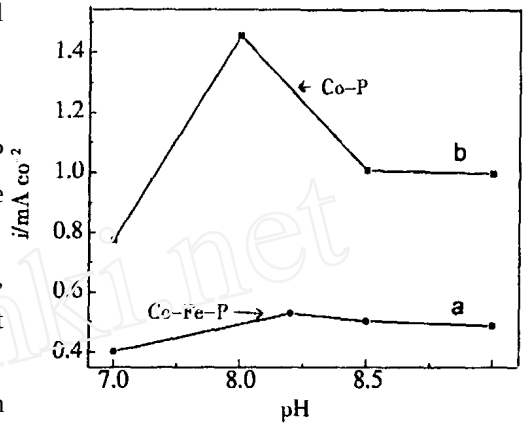

Fig. 7　Dependence of current density on the eletrolyte pH for Co-Fe-P (a) and Co-P (b), Components of the cathodic/anodic solution same as in Fig. 6

The electrochemical polarization experiments leads to the following results:

1) Ferrous sulphate in the solution affects both the cathodic and the anodic polarization processes, which reduces the deposition current and the potential. "The rate determining process" in these processes changes from the anodic reaction to "the mixed determining process" with the increase of concentration of ferrous sulphate.

2) The current density, i.e., the deposition rate for Co-Fe-P or for Co-P increases with the increase of pH of solution range from 7.0 to 7.7 or 7.5, then, decreases with it.

3) The results of the electrochemical polarization experiments basically accord with that of the electroless deposition rate measurements.

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硫酸亚铁对化学沉积钴-铁-磷合金中的影响

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摘要: 在以次亚磷酸钠为还原剂、硼酸为缓冲剂和柠檬酸钠为络合剂的碱性介质中, 化学沉积钴-铁-磷合金和钴-磷合金. 研究了沉积工艺, 如 pH 值和主盐 $CoSO_4$/ $FeSO_4$的摩尔比对沉积速率的影响. 发现镀液中的硫酸亚铁对钴-铁-磷合金沉积有阻碍作用, 以致其沉积速率比钴-磷的低. 电化学极化实验表明, 硫酸亚铁既影响阳极过程又影响阴极过程, 它降低了两者的极化电流和极化电势. 电化学实验结果与沉积速度测量结果基本相符.

关键词: 化学沉积; 合金; 钴; 铁; 电化学极化

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