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Role of the Intermediate Layer and Factors Determining Chemical Composition of the Film in the Electroless Ferrite-plating

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This paper describes electroless ferrite-plating on a Cu substrate whose surface is oxidized (the Cu-oxide layer works as an intermediate layer for the plating). Electron-diffraction and cathodic-reduction analyses showed that a Fe_3O_4 thin layer is formed on the intermediate layer during the initial reaction of the plating. This thin layer grows by the repetition of the adsorption of metal ions to the surface of the layer and the oxidation of the adsorbed Fe^{II} ions. Based on the adsorption-equilibrium of the metal ions on the surface of the film, the relationship between the composition of the metal ions adsorbed and that of the metal ions incorporated into the Co-ferrite film was formulated in terms of the concentrations of the metal ions in the reaction solution and the reaction pH. The analysis of the experimental data with this equation showed that the Co^{II} ions are more readily incorporated into the ferrite layer, as the mol ratio of the adsorbed Co^{II} ions to adsorbed iron ions ($R_{ads.}$) increases, but that a higher $R_{ads.}$ becomes unfavorable for the incorporation.

Recently, we reported a new method which enables the formation of crystalline-spinel film in an aqueous solution at low temperatures (below 80 °C).[1,2] Ferrite films are formed on the substrates by the oxidation of a mixed suspension of Fe^{II} and other metal ions (M^{n+}) in which the substrates are soaked. We can use various oxidizing agents such as air ("the air-bubbling method"), nitrate ion, hydrogen peroxide *etc.*, and anodic current. Thus, our method is a kind of electroless (chemical) plating or electro-plating. In the electroless ferrite plating on the poly(ethylene terephthalate)(PET) and stainless-steel substrates, an intermediate layer (an oxide layer of chemically plated copper or electro-plated Fe_3O_4) is required.[1,2]

The purposes of the present paper are 1) to clarify the initial reaction occurring on the intermediate layer of copper oxide in the electroless ferrite plating, and 2) to study the relationship between the adsorption behavior of the metal ions and the composition of the ferrite films formed during the electroless plating. For the performance of the study on the latter subject, we have devised a specially designed apparatus. We call the method using this apparatus, "the rotating-disc method."

Experimental

Chemicals and Substrates. Chemical reagents of analytical grade were used. NaOH solutions were prepared by dissolving NaOH in distilled water free from CO_2 and O_2. Copper sheets (30 μm×10×20 mm) whose surface had been oxidized in air at 160 °C for 30 min, were used as substrates.

Experiment of the Initial Reaction. After passing nitrogen gas into the solution containing Fe^{II} ions (17 mmol dm^{-3}, pH 7.0, T=70 °C) for 2 h, the Cu-substrate was dipped in the solution for 30 s—2h under a nitrogen atmosphere. The electron-diffraction pattern and cathodic-reduction curves of the oxides formed on the substrate were taken. The cathodic-reduction curves were taken using a Beckman Electroscan Model 30, applying a DC current at 10 A cm^{-1} in a stagnant borate buffer solution (pH 8.4, consisting of equal volumes of 0.075 mol dm^{-3} $Na_2B_4O_7\cdot 10H_2O$ and 0.075 mol dm^{-3} H_3BO_3 solutions) at 25 °C under a slow nitrogen gas stream. The borate buffer solution was deaerated before the measurement by passing nitrogen gas for several hours.

The Rotating-disc Method. A specially designed

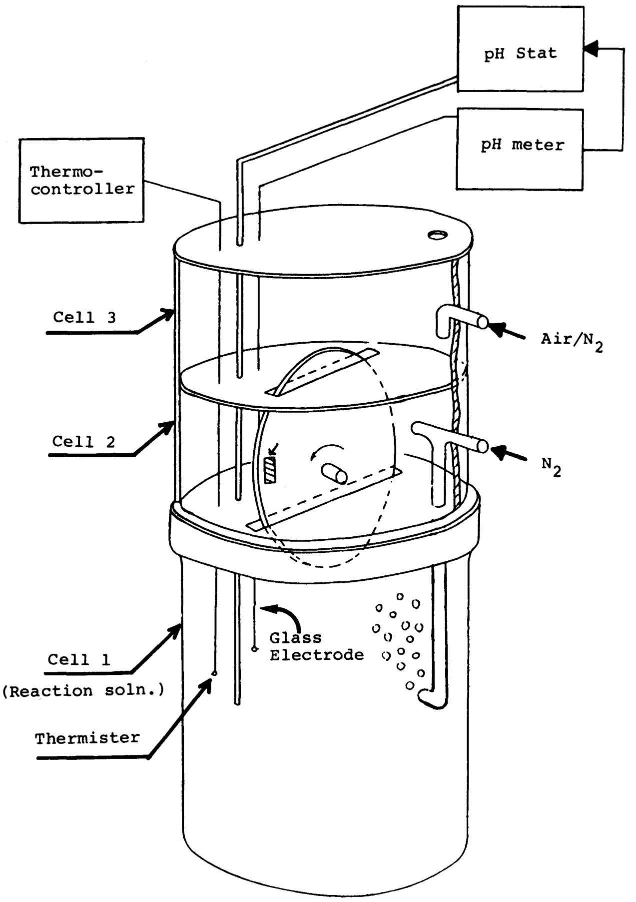


Fig. 1. The improved apparatus used for the chemical ferrite-plating.

apparatus (as illustrated in Fig. 1) was used. It is composed of three separated cells of a reaction solution (cell-1), an N_2 ambient to screen the reaction solution from oxygen (cell-2), and an air/N_2 (1:50) ambient (cell-3).

The Cu-substrates were mounted on the disc, and Cell number 1 was filled with about 1 dm^3 of distilled water through which nitrogen gas had been passed for 1 h to remove any dissolved oxygen. Nitrogen gas was passed through all the cells. After raising the temperature of the water in cell 1 to 70 °C, $FeCl_2 \cdot 3.5H_2O$ and $CoCl_2 \cdot 6H_2O$ were dissolved (Fe^{II}; 5.2 mmol dm^{-3}, Co^{II}; 0—15 mmol dm^{-3}). The pH was adjusted to a desired value (6.0—7.5) by adding an NaOH solution, and then the disc was rotated at 50—60 min^{-1}. After 5 min, the air/N_2 gas (1:50) was passed through cell 3 in place of nitrogen gas. After 2 h, the rotation of the disc was stopped, and the substrates were removed from the disc. The phase of the film was examined by electron and X-ray diffraction methods.

In "the rotating-disc method", the oxidation reaction takes place only on the surface of the substrate in cell 3, and a little amount of the metal ions are consumed during the formation of the ferrite film. Therefore, the concentrations of the metal ions in the reaction solution can be kept constant during the reaction. The thickness of the film was estimated by the chemical analysis of the film, assuming the chemical formula of $(Fe, Co)_{3.00}O_{4.00}$ and the density equal to that for $CoFe_2O_4$.

Chemical Anaylsis. Iron and cobalt contents in the ferrite films were determined by the atomic absorption method after dissolving the films in an HCl solution (1:1).

Results and Discussion

Formation of a Thin Fe_3O_4 Layer on the Cu-substrate in the Initial Reaction. The electron-diffraction

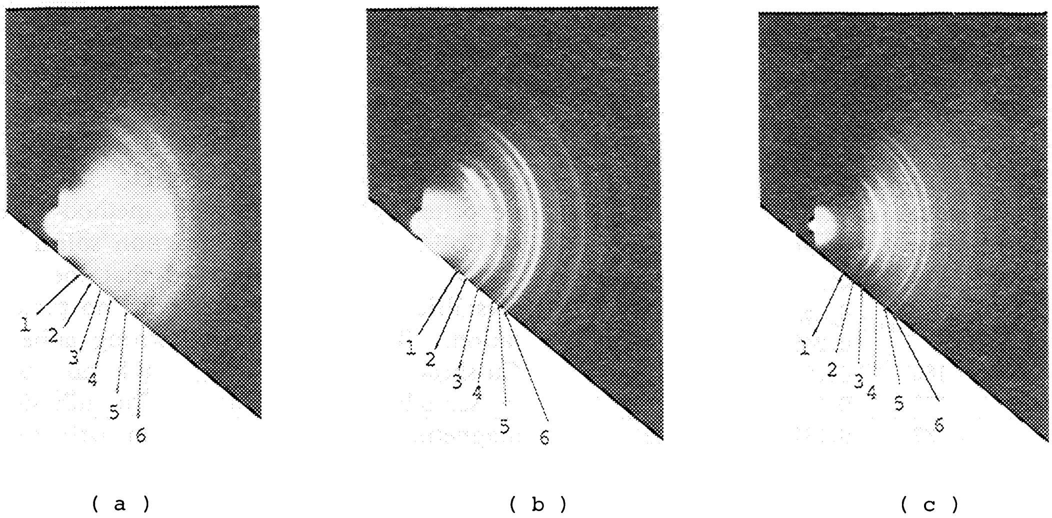


Fig. 2. Electron diffraction photographs for (a) the surface coating as formed on the Cu-sheet, (b) the Fe_3O_4 layer top coating formed on the Cu-oxide coating, and (c) a Co-ferrite film ($Co_{0.3}Fe_{2.7}O_4$) prepared by the rotating-disc method.

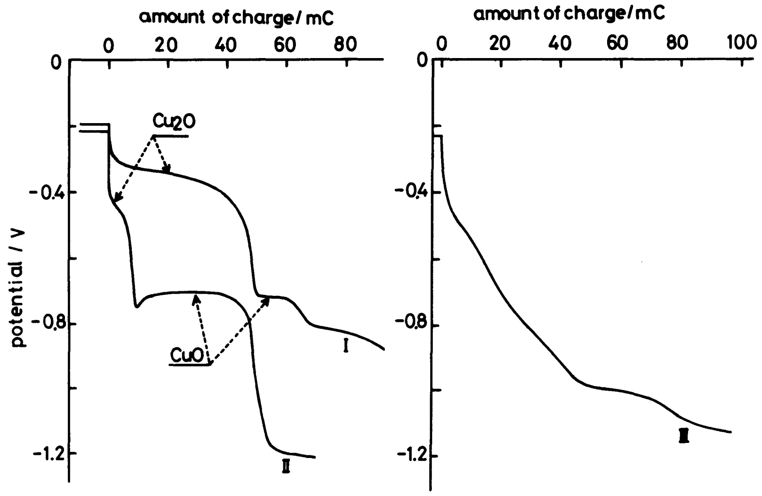


Fig. 3. Cathodic reduction curves for (a) the surface coating as formed on the Cu-sheet by heating in air at 160 °C for 10 min. (curve I) and 30 min. (curveII), and (b) the Fe_3O_4 top coating formed on the Cu-oxide coating.

pattern (Fig. 2a) and the *d* values (Table 1a) showed that the surface of the Cu-substrate was covered with oxide layers of Cu_2O and CuO. Curves I and II in Fig. 3a show the cathodic-reduction curves of the coatings formed on the Cu-substrate by heating in air at 160 °C for 10 and 30 min, respectively. They show two plateaus at the potential characteristic of CuO and Cu_2O, respectively. The ratio of CuO/Cu_2O increases as the heating time increases from 10 to 30 min. When the Cu-substrate with the Cu-oxide coating (30 min oxidation) was soaked in the reaction solution containing Fe^{II} ion (17 mmol dm^{-3}) at pH 7.0 and 70 °C under a nitrogen atmosphere for 30 s, a thin Fe_3O_4 layer was formed on the Cu-sheet substrate, as shown by the electron diffraction data and the cathodic-reduction measurement of Fig. 2b, Table 1b, and Fig. 3b. The layer was very thin; strong metallic copper color appeared through the film (its thickness could not be measured). This reaction was completed almost instantly; the thin Fe_3O_4 layer did not grow any more, even though the dipping time was extended to 2 h. It is assumed that the Fe^{II} ions are oxidized on the surface of the Cu-oxide layer, and that the thin Fe_3O_4 layer is deposited on its surface. This reaction will stop when the surface of the Cu-sheet substrate is completely covered with the thin Fe_3O_4 layer. This would be the cause for the formation of the thin layer. The formation of ferrite films (or particles) in the aqueous solution proceeds in two stages;[1-4] 1) the adsorption of the metal ions to the solid surface, and 2) the ferrite-formation with the oxidation of Fe^{II} ions to Fe^{III}. The Cu-oxide coating on the Cu-sheet substrate exhibits the activity of not only adsorbing the ions but also oxidizing Fe^{II} into Fe^{III}, thus forming the thin Fe_3O_4 layer.

Table 1. The "*d*"-values observed in the electron diffraction patterns of Figs. 1(a), (b), and (c), which are compared to literature values obtained by X-ray diffractometry for Cu-oxides, Fe_3O_4, and $CoFe_2O_4$, respectively

(a) No. in Fig. 2(a)	d observed nm	d Cu_2O[a] and CuO[b] nm		(*hkl*)
1	0.300	0.3020	Cu_2O	(110)
2	0.254	0.2530	CuO	(002)
		0.2523	CuO	$(\bar{1}11)$
		0.2465	Cu_2O	(111)
3	0.186	0.1866	CuO	$(\bar{2}02)$
4	0.159	0.1581	CuO	(202)
5	0.137	0.1375	CuO	(220, 113)
6	0.127	0.1287	Cu_2O	(311)

(b) No. in Fig. 2(b)	d observed nm	d Fe_3O_4[c] nm	(*hkl*)
1	0.301	0.2967	(220)
2	0.254	0.2532	(311)
3	0.211	0.2099	(400)
4	0.171	0.1715	(422)
5	0.162	0.1616	(511, 333)
6	0.149	0.1485	(440)

(c) No. in Fig. 2(c)	d observed nm	d $CoFe_2O_4$[d] nm	(*hkl*)
1	0.309	0.296	(220)
2	0.261	0.2531	(311)
3	0.216	0.2099	(400)
4	0.173	0.1713	(422)
5	0.163	0.1615	(511, 333)
6	0.150	0.1483	(440)

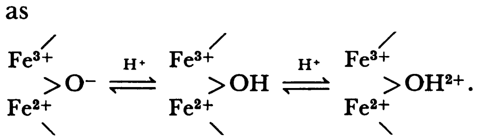
a) ASTM X-ray Data Card 5-667, b) 5-661, c) 19-629, d) 22-1086.

Formation of Co-ferrite Films on the Cu-substrate by "the Rotating-disc Method." Figure 2c and Table 1c show the results of the electron diffractometry on the Co-ferrite film ($Co_{0.3}Fe_{2.7}O_4$, 370 nm thickness) deposited by "the rotating-disc method" (the mol ratio of $Co^{II}/Fe^{II}=0.50$ in the reaction solution, pH 7.0). X-ray diffractometry showed that the film has the crystallized spinel structure with no preferred orientation. This film showed strong adhesion to the Cu-sheet substrate, and could not be detached by scratching with a nail. The adhesion and the magnetic property of the film will be published elsewhere.[5] Co-ferrite films with various compositions ($Co_xFe_{3-x}O_4$, $x=0.10$—0.52; the oxidation state of the Co-ferrite film is not unequivocal) were plated on the Cu-substrate in the pH range of 6.5—7.5 and at the mol ratios of $[Co^{II}]/[Fe^{II}]=$ 0.5—3.0 in the reaction solution. At pH 5.5, where little amount of the metal ions of Fe^{II} and Co^{II} are adsorbed,[3] no Co-ferrite films were deposited, although we used the substrate whose surface had been oxidized.

The reaction mechanism of the formation of the Co-ferrite film is considered as follows: When the substrate is dipped into the reaction solution (pH 7.0), Fe^{II} and Co^{II} ions are adsorbed on the surface of the Cu-oxide coating. When some of the adsorbed Fe^{II} ions are oxidized by Cu-oxide, the metal ions (Fe^{II}, Fe^{III}, Co^{II}) on the surface are transformed into a Co-ferrite, forming a thin ferrite layer on the surface. The ferrite layer, thus formed, can adsorb the Co^{II} and Fe^{II} ions. Some of the adsorbed Fe^{II} ions are oxidized by oxygen in cell 3, and a new Co-ferrite layer is formed. These adsorption-oxidation reactions are repeated by rotating the disc, which results in the growth of the ferrite layer.

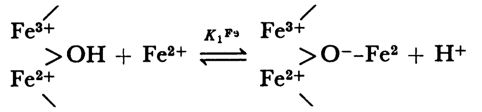
The adsorption reaction occurs at a higher rate than that of the ferrite-formation reaction;[3] the adsorption reaction is the rate-determining step. Furthermore, in "the rotating-disc method", the concentrations of the metal ions in the reaction solution (cell-1) are kept constant. This means that, in "the rotating-disc method", the chemical composition of the ferrite film can be discussed based on the adsorption-equilibrium of the metal ions in terms of the concentrations of the metal ions and the reaction pH.

Effect of Concentrations of Metal ions in the Reaction Solution and the Reaction pH on the Composition of the Co-ferrite Films. We assume here that a layer of ferrite, say Fe_3O_4, has been already formed on the oxide coating of the substrate. The OH group at the solid/liquid interface exhibits an amphoteric property, as



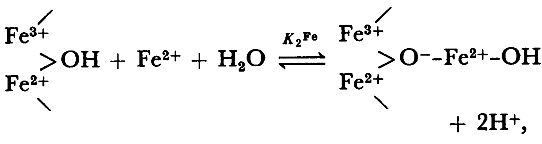
$$\begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>O^-}\\ \mathrm{Fe^{2+}}\end{array} \overset{\mathrm{H^+}}{\rightleftharpoons} \begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>OH}\\ \mathrm{Fe^{2+}}\end{array} \overset{\mathrm{H^+}}{\rightleftharpoons} \begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>OH^{2+}}.\\ \mathrm{Fe^{2+}}\end{array} \qquad (1)$$

The OH group works as the adsorption site for the metal ions. In general, there are two types of adsorption, *i.e.*, those unaccompanied and accompanied by hydrolysis: For the Fe^{2+} ions



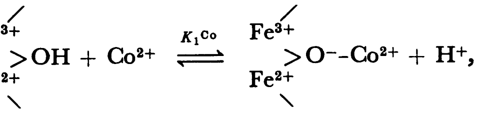
$$\begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>OH}\\ \mathrm{Fe^{2+}}\end{array} + \mathrm{Fe^{2+}} \overset{K_1^{\mathrm{Fe}}}{\rightleftharpoons} \begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>O^-\text{-}Fe^{2}}\\ \mathrm{Fe^{2+}}\end{array} + \mathrm{H^+} \qquad (2a)$$

and



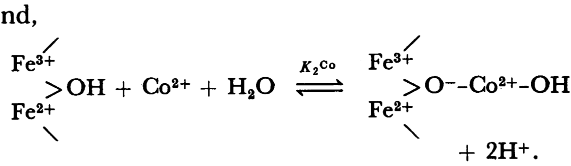
$$\begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>OH}\\ \mathrm{Fe^{2+}}\end{array} + \mathrm{Fe^{2+}} + \mathrm{H_2O} \overset{K_2^{\mathrm{Fe}}}{\rightleftharpoons} \begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>O^-\text{-}Fe^{2+}\text{-}OH^-}\\ \mathrm{Fe^{2+}}\end{array} + 2\mathrm{H^+}, \qquad (2b)$$

and for the Co^{2+} ions,



$$\begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>OH}\\ \mathrm{Fe^{2+}}\end{array} + \mathrm{Co^{2+}} \overset{K_1^{\mathrm{Co}}}{\rightleftharpoons} \begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>O^-\text{-}Co^{2+}}\\ \mathrm{Fe^{2+}}\end{array} + \mathrm{H^+}, \qquad (2a')$$

and,



$$\begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>OH}\\ \mathrm{Fe^{2+}}\end{array} + \mathrm{Co^{2+}} + \mathrm{H_2O} \overset{K_2^{\mathrm{Co}}}{\rightleftharpoons} \begin{array}{l}\mathrm{Fe^{3+}}\\ \quad\mathrm{>O^-\text{-}Co^{2+}\text{-}OH^-}\\ \mathrm{Fe^{2+}}\end{array} + 2\mathrm{H^+}. \qquad (2b')$$

Here, K_1^{Fe} and K_2^{Fe} (K_1^{Co} and K_2^{Co}) are the equilibrium constants for the adsorption of the Fe^{2+} (Co^{2+}) ions. The adsorption unaccompanied by the hydrolysis (Eqs. 2a and 2a′) dominates when the pH of the solution is low, while that accompanied by the hydrolysis (Eqs. 2b and 2b′) dominates when the pH is high.[6] When some of the Fe^{II} ions [adsorbed following Eqs. 2a and 2b] are oxidized, the ions on the surface (Fe^{II}, Fe^{III}, and Co^{II}), both hydrolyzed and unhydrolyzed, are transformed into spinel ferrite.

In the rotating-disc method, the concentrations of the Fe^{II} and Co^{II} ions in the solution are kept constant. In the pH range studied here (6—7.5), almost all of the Fe^{II} and Co^{II} ions in the solution are Fe^{2+} and Co^{2+}. Therefore, the equilibrium constants for the adsorption of the ions are expressed in terms of the concentrations in the reaction solution of cell-1 (Fig. 1) as follows:

For Eqs. 2a and 2b,

$$K_1^{\mathrm{Fe}} = [\mathrm{>O^-\text{-}Fe^{2+}}][\mathrm{H^+}]/([\mathrm{Fe^{2+}}][\mathrm{>OH}]), \qquad (3a)$$

$$K_2^{\mathrm{Fe}} = [\mathrm{>O^-\text{-}Fe^{2+}\text{-}OH^-}][\mathrm{H^+}]^2/([\mathrm{Fe^{2+}}][\mathrm{>OH}]), \qquad (3b)$$

and for Eqs. 2a′ and 2b′,

$$K_1^{\mathrm{Co}} = [\mathrm{>O^-\text{-}Co^{2+}}][\mathrm{H^+}]/([\mathrm{Co^{2+}}][\mathrm{>OH}]), \qquad (3a')$$

$$K_2^{\mathrm{Co}} = [\mathrm{>O^-\text{-}Co^{2+}\text{-}OH^-}][\mathrm{H^+}]^2/([\mathrm{Co^{2+}}][\mathrm{>OH}]). \qquad (3b')$$

Here, $[H^+]$, $[Fe^{2+}]$, and $[Co^{2+}]$ are the concentrations of the respective ions in the solution, $[>OH]$ is that of the adsorption site, and $[>O^--Fe^{2+}]$,$[>O^--Fe^{2+}-OH^-]$, $[>O^--Co^{2+}]$, and $[>O^--Co^{2+}-OH^-]$ are those of the Fe^{II} and Co^{II} ions adsorbed without and with the hydrolysis*, respectively.

The ratio of the adsorbed Co^{II} ions to the adsorbed Fe^{II} ions is given by

$$\begin{aligned} \mathrm{R_{ads.}} &= (\mathrm{Co/Fe})_{\mathrm{ads.}} \\ &= ([\mathrm{>O^-\text{-}Co^{2+}}] + [\mathrm{>O^-\text{-}Co^{2+}\text{-}OH^-}])/ \\ &\quad ([\mathrm{>O^-\text{-}Fe^{2+}}] + [\mathrm{>O^-\text{-}Fe^{2+}\text{-}OH^-}]) \end{aligned} \qquad (4)$$

Using Eqs. 3a—3b′, we can substitute the adsorbed-ion concentrations in Eq. 4 with the ion concentrations in the reaction solution as

$$\begin{aligned} R_{\mathrm{ads.}} = {} & ([\mathrm{Co^{2+}}]/[\mathrm{Fe^{2+}}])(K_1^{\mathrm{Co}}[\mathrm{H^+}]+K_2^{\mathrm{Co}})/ \\ & (K_1^{\mathrm{Fe}}[\mathrm{H^+}]+K_2^{\mathrm{Fe}}). \end{aligned} \qquad (5)$$

Now, we introduce a ratio, t, as

$$t = R_{\mathrm{film}}/R_{\mathrm{ads.}}, \qquad (6)$$

where R_{film} is the mol ratio of Co^{II} to Fe_{total} in the ferrite film. From Eqs. 5 and 6, we obtain

$$\log R_{\mathrm{film}} = \log\frac{[\mathrm{Co^{2+}}]}{[\mathrm{Fe^{2+}}]} + \log\left(t\frac{K_1^{\mathrm{Co}}[\mathrm{H^+}]+K_2^{\mathrm{Co}}}{K_1^{\mathrm{Fe}}[\mathrm{H^+}]+K_2^{\mathrm{Fe}}}\right) \qquad (7)$$

which expresses R_{film} as a function of $[Co^{2+}]/[Fe^{2+}]$, t, and the pH. Figure 4 shows the relationship between log R_{film} and pH at $[Co^{2+}]/[Fe^{2+}]=0.50$, 0.75, and 3.0. The composition of the ferrite film (R_{film}) increases linearly with an increase in the reaction pH at a given mol ratio of $[Co^{2+}]/[Fe^{2+}]$. Thus, the second term of the right side in Eq. 7 varies linearly with the reaction pH (the 1st term is constant for each curve.)

Here, we discuss the ratio t. Assuming that t at $[Co^{2+}]/[Fe^{2+}]=3.0$ (Curve A in Fig. 4) as t_0, and those for 0.75 and 0.5 (Curves B and C in Fig. 4) as t_n, we can calculate t_n/t_0 for various pH values

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* The concentrations of the ions, *i.e.*, $[H^+]$, $[Fe^{2+}]$, and $[Co^{2+}]$, are expressed in the unit of mol/volume, while those of the adsorption sites and the adsorbed ions, *i.e.*, $[>OH]$, $[>O^--Fe^{2+}-OH^-]$, $[>O^--Co^{2+}]$, *etc.*, are in number/area.

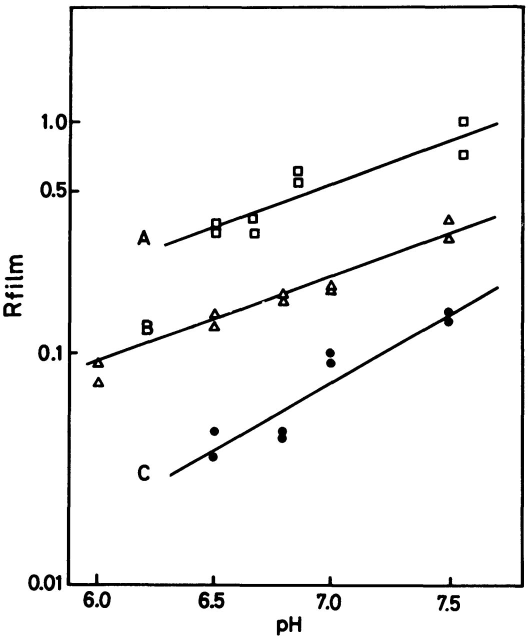

Fig. 4. The pH dependence of the atomic ratio ($R_{\text{film}} = \text{Co/Fe}$) of the films prepared by the rotaing-disc method using the solutions with the ion ratios of $[\text{Co}^{\text{II}}]/[\text{Fe}^{\text{II}}]=3.0$ (Curve A), 0.75 (B), and 0.50 (C).

using Eq. 7. When the t_n/t_0 is k_n, Eq. 6 is rewritten as

$$\log R_{\text{film}}/k_n = \log R_{\text{ads.}} + \log t_0. \qquad (8)$$

Since t_0 is constant for a given pH value, Eq. 8 shows that the change in the value of log R_{film}/k_n at constant pH value is that in the value of R_{ads}. Thus, for a given reaction pH, the relationship between k_n and R_{film}/k_n will give how the R_{ads}. affects the incorporatation of the Co^{II} ions into the ferrite layer. This is given by Fig. 5. As can be seen here, the Co^{II} ions are more readily incorporated into the ferrite layer, as the mol ratio of the adsorbed Co^{II} ions to the adsorbed iron ions ($R_{\text{ads.}}$) increases. However, a higher $R_{\text{ads.}}$ becomes unfavorable for the incorporation.

Conclusion

(1) In the initial reaction of the electroless ferrite-plating, the intermediate layer of the Cu-oxide adsorbs the metal ions and oxidizes the adsorbed Fe^{II} ions, and a thin ferrite-layer is formed on the surface.

(2) Co-ferrite films ($\text{Co}_x\text{Fe}_{3-x}\text{O}_4$, $x=0.10$—0.52) were plated on the Cu-substrate with the intermediate layer of the Cu-oxides by "the rotating-disc method" in the pH range 6.5—7.5 and at the mol ratios of $[\text{Co}^{\text{II}}]/[\text{Fe}^{\text{II}}]=0.5$—$3.0$ in the reaction solution (T=70 °C).

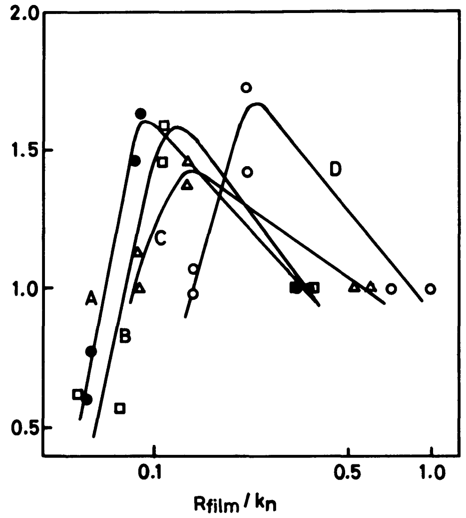

Fig. 5. The relationship between k_n and R_{film}/k_n at pH 6.5 (Curve A), 6.8(B), 7.0(C), and 7.5(D).

(3) Based on the adsorption-equilibrium of the metal ions on the surface of the film, the relationship between the composition of the metal ions adsorbed and that of the metal ions incorporated into the Co-ferrite film was formulated in terms of the concentrations of the metal ions in the reaction solution and the reaction pH. The analysis of the experimental data with this equation showed that the Co^{II} ions are more readily incorporated into the ferrite layer, as the mol ratio of the adsorbed Co^{II} ions to adsorbed iron ions ($R_{\text{ads.}}$) increases, but that a higher $R_{\text{ads.}}$ becomes unfavorable for the incorporation.

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