

## Conditions for Synthesizing Magnetite Films at Room Temperature by Ferrite Plating: Discussion Based on Equilibrium Kinetics

Kazuhiro Nishimura, Yoshihisa Kohara, Yoshitaka Kitamoto, and Masanori Abe

Department of Physical Electronics, Tokyo Institute of Technology

O-okayama, Meguro-ku, Tokyo, 152-8552, Japan

Fax: 81-3-5734-2199, e-mail: knishim@pe.titech.ac.jp

Magnetite ( $\text{Fe}_3\text{O}_4$ ) films are successfully grown at room temperature ( $24^\circ\text{C}$ ) by ferrite plating in which aqueous  $\text{Fe}^{2+}$  ions are oxidized by  $\text{NaNO}_2$  at  $\text{pH}=7.7\sim 8.9$ . The  $\text{pH}$  is increased from that ( $5\sim 7$ ) at which previous  $\text{Fe}_3\text{O}_4$  plating was performed at higher temperature  $60\sim 100^\circ\text{C}$ , following the “guiding principle” obtains in our previous study [K. Nishimura et al., *J. Magn. Soc. Jpn.*, **24** (1999)]. Conditions on which single-phase magnetite films are synthesized are plotted as a two-dimensional phase diagram of  $\text{pH}$  of the  $\text{Fe}^{2+}$  solution and the concentration of the oxidizing solution of  $\text{NaNO}_2$ . The conditions are examined in terms of the phase equilibrium in the  $\text{Fe}^{2+}/\text{Fe}_3\text{O}_4$  boundary including the  $\text{NO}_2^-$  ions.

Key words: ferrite plating, magnetite film, room-temperature synthesis, phase equilibrium

### 1. INTRODUCTION

By ferrite plating, in which adsorption of metal ions and aqueous  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  oxidation play an essential role, we can synthesize polycrystalline ferrite films of spinel type,  $(\text{M}, \text{Fe})_3\text{O}_4$  where  $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$ , etc., directly from an aqueous solution at  $60\sim 100^\circ\text{C}$ . Thus ferrite plating can use, as substrates, materials with low heat-resistance (e.g. plastics, organic fibers, GaAs integrated circuits, etc.). Therefore, ferrite plating has attracted much interest as a technique which facilitates fabrication of new magnetic-thin-film devices on non-heat-resistant substrates. If we can lower the temperature of ferrite plating further down to room temperature, we will be able to fabricate novel electronic and biomedical magnetic devices in which layers of very low heat-resistance polymers (such as organic lipids, proteins including enzymes, etc.) are used as substrates and/or

insulating layers. Also the organic polymer layers may function as templates which stimulate growth of ferrite single crystals as observed in biomineralization of inorganic materials<sup>2</sup>.

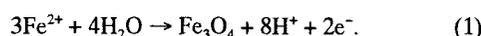
In our previous studies we examined the temperature dependence<sup>3</sup> of the  $\text{Fe}^{2+}/\text{Fe}_3\text{O}_4$  boundary line in the potential- $\text{pH}$  diagram<sup>4</sup>, along which ferrite plating is performed. And we noticed that the room temperature ferrite plating might be facilitated by elevating  $\text{pH}$  value of reaction solution. Following this “guiding principle,” we successfully synthesized  $\text{Fe}_3\text{O}_4$  (magnetite) films at  $24^\circ\text{C}$  using as oxidizing reagents either anodic current (electro-ferrite plating)<sup>5</sup> or  $\text{NaNO}_2$  (electroless ferrite plating)<sup>6</sup>.

Our previous reports<sup>6</sup> on the room temperature  $\text{Fe}_3\text{O}_4$  film synthesis laid emphasis mainly on experiments and characterizations (of magnetic and crystallographic

properties) for the prepared films. In this paper we will describe in detail how the guiding principle is derived and discuss the experimental results (i.e. conditions on which room temperature synthesis is attained) in terms of chemical thermodynamics.

## 2. GUIDING PRINCIPLE FOR ROOM-TEMPERATURE MAGNETITE FILM SYNTHESIS

The synthesis of  $\text{Fe}_3\text{O}_4$  (solid) from aqueous  $\text{Fe}^{2+}$  ions by ferrite plating is formulated as follows,



The equilibrium potential for the reaction expressed by Eq. (1) at temperature  $T$  is given by the following Nernst equation as<sup>3,4</sup>,

$$E = \frac{\Delta F^0}{2F} - \frac{3RT}{2F} \ln(\gamma_{\text{Fe}^{2+}} \cdot c_{\text{Fe}^{2+}}) - \frac{9.212RT}{F} \text{pH} \cdot (2)$$

$\Delta F^0$ : change in the standard free energy

$\text{pH}$ : hydrogen ion concentration

$\gamma_{\text{Fe}^{2+}}$ : activity constant of  $\text{Fe}^{2+}$

$c_{\text{Fe}^{2+}}$ : concentration of  $\text{Fe}^{2+}$

$F$ : Faraday constant

$E$ : potential vs. normal hydrogen electrode

$R$ : ideal gas constant

For a dilute solution of  $C(\text{Fe}^{2+})=10^{-6}\text{mol/l}$ , where  $\gamma(\text{Fe}^{2+})=1$  holds, Eq. (2) is calculated at room temperature

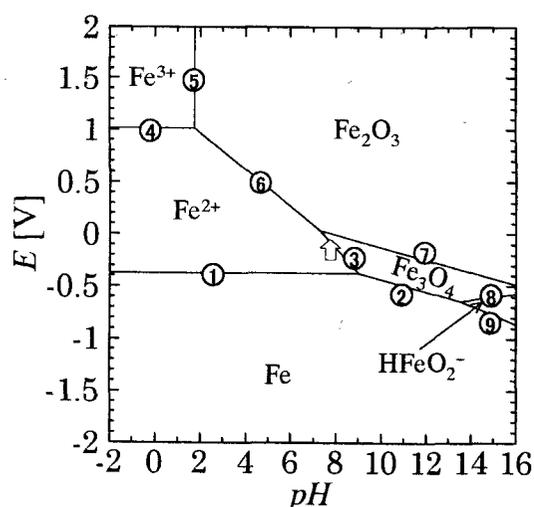


Fig. 1 Potential- $\text{pH}$  diagram for iron<sup>4</sup> at 298K.

(298K) as the boundary line ③ shown in Fig.1 by Pourbaix<sup>4</sup>.

Figure 1 shows the phase equilibrium at 25°C, a temperature lower than those (60-100°C) at which our previous plating experiments were performed. Therefore, in order to elucidate the guiding principle for the room temperature synthesis, we calculated the phase boundary, or Eq. (2), at 60 and 100°C. We put  $C(\text{Fe}^{2+})=3.0 \times 10^{-2}\text{mol/l}$ , the actual concentration in our experiments which is much higher than that ( $C(\text{Fe}^{2+})=10^{-6}\text{mol/l}$ )<sup>4</sup>. The calculated boundary line ③ (Eq. (2)), as well as the values for  $\Delta F^0$  used for the calculation, is given in Table 1. The  $\text{Fe}^{2+}/\text{Fe}_3\text{O}_4$  equilibrium boundary line shifts to high  $\text{pH}$  region as temperature decreases from the higher values to room temperature, as shown in Fig.2. Thus we attained the guiding principle that the room temperature synthesis might be realized by increasing  $\text{pH}$  of the aqueous solution.

Table 1 Change in the standard free energy (taken from the literature<sup>3</sup>), and the boundary line ③ (i.e. Eq. (2)) calculated in this study at various temperatures.

Temperature	$\Delta F^0$	Boundary line ③
298 K (25°C)	189400	$E = 1.12 - 0.236 \text{pH}$
333 K (60°C)	177900	$E = 1.07 - 0.264 \text{pH}$
373 K (100°C)	165600	$E = 1.03 - 0.296 \text{pH}$

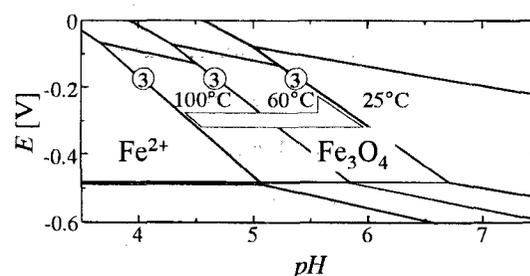


Fig. 2  $\text{Fe}^{2+}/\text{Fe}_3\text{O}_4$  equilibrium boundary lines in a potential- $\text{pH}$  diagram for iron at various temperatures.

## 3. RESULTS AND DISCUSSIONS

Following the guiding principle, we performed room-temperature (24°C) ferrite plating of  $\text{Fe}_3\text{O}_4$  at

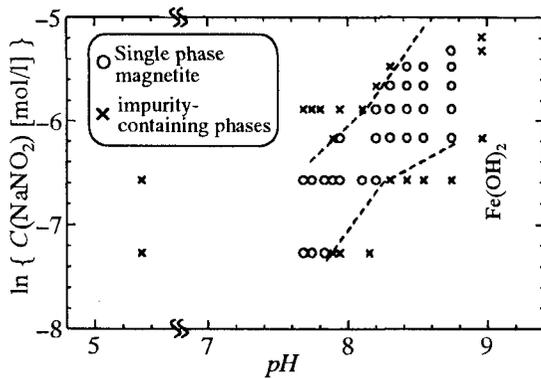


Fig. 3 Phase diagram of plated ferrite films, plotted vs.  $pH$  and  $\ln \{C(\text{NaNO}_2)\}$ . Circles show single-phase magnetite and crosses show impurity-containing phases.

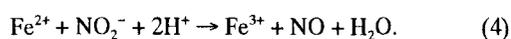
elevated  $pH$  (7.68~8.96). We used  $\text{FeCl}_2 + \text{NH}_3$  ( $pH=5.33\sim 8.96$ ) as a reaction solution to which an oxidizing solution of  $\text{NaNO}_2$  was added. We used glass plates as substrates and performed the plating for 3 hours. Details of the experiments are described elsewhere<sup>5</sup>.

Figure 3 shows the resultant phase diagram of the plated films, plotted vs.  $pH$  of mixed solution and logarithmic concentration of  $\text{NaNO}_2$ ,  $\ln \{C(\text{NaNO}_2)\}$ . Single phase  $\text{Fe}_3\text{O}_4$  films, as revealed by X-ray diffractometry, are obtained at  $pH$  higher than 7.68, as predicted by the guiding principle. In the previous plating at higher temperatures (60~100°C), films of single phase  $\text{Fe}_3\text{O}_4$  are obtained in a lower  $pH$  region of 5~6.8.

To compare the results shown in Fig.3 with the calculation shown in Fig.2, we must take the oxidizing reaction of  $\text{NaNO}_2$  into account.  $\text{NaNO}_2$  is dissociated into ions in the aqueous solution as



The resultant  $\text{NO}_2^-$  ions oxidize  $\text{Fe}^{2+}$  in the following way,



Combining Eq. (4) and Eq. (1) gives,

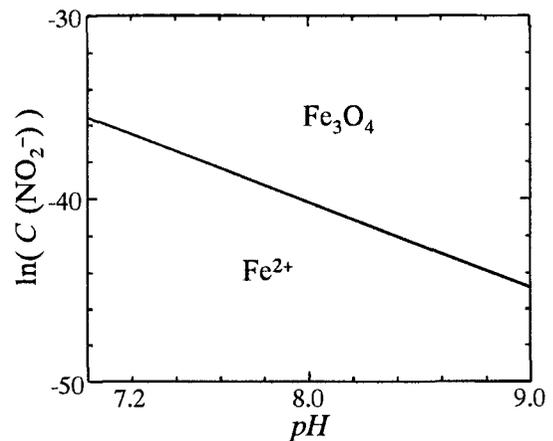
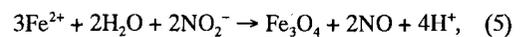


Fig.4  $\text{Fe}^{2+}/\text{Fe}_3\text{O}_4$  equilibrium boundary line in an equation (6).

Table 2 Standard chemical potentials at 298K<sup>4,7</sup>.

Formula	$\mu_i^0$ [kJ/mol]
$\text{Fe}^{2+}$	-84.94
$\text{Fe}_3\text{O}_4$	-1014.23
$\text{NO}_2^-$	-34.52
$\text{NO}$	86.69
$\text{H}^+$	0
$\text{H}_2\text{O}$	-237.20



from which we obtain

$$\ln c_{\text{NO}_2^-} = \frac{\Delta F^0}{2RT} - \frac{3}{2} \ln c_{\text{Fe}^{2+}} - 4.606 pH \quad (6a)$$

$$\Delta F^0 = \mu_{\text{Fe}_3\text{O}_4}^0 + 2\mu_{\text{NO}}^0 - 3\mu_{\text{Fe}^{2+}}^0 - 2\mu_{\text{H}_2\text{O}}^0 - 2\mu_{\text{NO}_2^-}^0 \quad (6b)$$

Here  $\Delta F^0$  is the change in the standard free energy, and  $\mu_i^0$  ( $i=\text{Fe}_3\text{O}_4, \text{NO}, \text{Fe}^{2+}$ , etc.) the respective standard chemical potentials<sup>4,7</sup>, the values for which are given in Table 2. At room temperature ( $T=298\text{K}$ ) and  $C(\text{Fe}^{2+})=3.0 \times 10^{-2} \text{mol/l}$  the  $\text{Fe}^{2+} / \text{Fe}_3\text{O}_4$  phase boundary line is calculated from Eq. (6) as shown in Fig.4. The boundary line appears in  $pH$  range (7~9) of actual experimental conditions. This means that the  $\text{Fe}_3\text{O}_4$  synthesis at room temperature utilizing the  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  oxidation by  $\text{NaNO}_2$  can be expressed by Eq. (6). However, the concentration of  $\text{NaNO}_2$  in Fig.4 is much lower than the experimental value (c.f. Fig.3), and the

$\text{Fe}^{2+} / \text{Fe}_3\text{O}_4$  boundary line has a negative slope while the observation gives a positive slope. This problem will be solved by considering

- (1) the effect of such spurious ions as  $\text{NH}_3^+$  and  $\text{Na}^+$  in the reaction solution, and
- (2) *pH* dependence of the adsorption rate of  $\text{Fe}^{2+}$  ions on the substrate surface which plays an essential role in ferrite plating.

We are continuing to investigate this problem.

Room temperature synthesis of magnetite will be also realized by spin spray ferrite plating<sup>8</sup>, in which *pH* value is kept unchanged by virtue of the *pH* buffer contained in the oxidizing solution.

#### 4. CONCLUSION

Examining the Nernst equation for the  $\text{Fe}^{2+} / \text{Fe}_3\text{O}_4$  phase boundary, we attained the guiding principle that  $\text{Fe}_3\text{O}_4$  synthesis at room temperature is realized by increasing *pH* of the reaction solution from that at which higher-temperature (60~100°C) plating was performed previously. Based on the principle we successfully synthesized the  $\text{Fe}_3\text{O}_4$  films at 24°C. In order to explain the resultant conditions for obtaining single-phase  $\text{Fe}_3\text{O}_4$  films, we must take into account the spurious ions (i.e.  $\text{NH}_3$  and  $\text{Na}^+$ ) and *pH* dependence of the adsorption rate of  $\text{Fe}^{2+}$ .

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