The Anisotropy of the Crystal Growth of Fe_3O_4 in an Aqueous Solution

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The anisotropy of the crystal growth of the spinel-type ferrites in an aqueous solution was studied using ferrite films piled up on the glass substrate by means of the thin liquid-film method (TLF method). From the difference between the values of the O_{ind} (the parameter for the degree of the oxidation state), it was found that the Fe_3O_4 crystal grows in the (111) direction in the "oxidation state" (O_{ind}=1.4×10^{-2} dm^3 min^{-1}), but in the (100) direction in the "Fe^{2+}-rich state" (O_{ind}=3.38×10^{-4}dm^3 min^{-1}). Although the reaction conditions for the formation of the Co(II)- and Zn(II)-ferrites were the same (both used in the "oxidation-state"; O_{ind}=5.5—5.8×10^{-2} dm^3 min^{-1}), the anisotropy of the crystal growth was different between Co^{2+} [the (111) direction] and Zn^{2+} [the (100) direction]. These results were explained in terms of difference in the degree of the oxidation state (O_{ind}). For the inverse spinel, the slower rate of the formation of the sublattice of the B site in the "oxidation-state" seems to cause the preferential formation of the A site, since the Fe^{3+} ions are preferentially incorporated into the A site. This results in the anisotropy in the (111) direction of Fe_3O_4 and Co(II)-ferrite (inverse spinel). On the contrary, in the "Fe^{2+}-rich state", the preferential formation of one of the two B sites (the Fe^{2+} occupies one of the two B sites in the inverse spinel) results in the anisotropy in the (100) direction of Fe_3O_4. For the normal spinel, the acceleration of the incorporation of the Fe^{3+} ions into the B site in the "oxidation-state" will result in the anisotropy in the (100) direction. This is the case for the anisotropy in the (100) direction of the Zn(II)-ferrite.

Ferrites are formed by the air oxidation of mixed hydroxides of Fe(II) and other metal ions (M^{n+}) in an aqueous solution at pH 7—11 and above 56 °C.[1—6)] We have been studying the reaction mechanism of the ferrite formation in aqueous solutions and have proposed the following mechanism:[7—11)] the ferrite crystal grows by the repetition of the 3 steps of: 1) the adsorption of Fe(II) ions on the surfaces of the ferrite particles, 2) the formation of a γ-FeO(OH) layer on the surface by means of the oxidation of the adsorbed Fe(II) ions, and 3) the formation of a ferrite-layer by means of the adsorption of the Fe(II) ion to the γ-FeO(OH) layer. Recently, we[12—15)] have succeeded in forming a thin ferrite film on such substrates as glass, plastics, metal oxides, and alumina-plates in aqueous solutions ("ferrite plating"). In this process, the ferrite films (300—5000 nm) are formed by the repetition of the 3 steps mentioned above. The ferrite film is very smooth and gives a distinct X-ray diffraction pattern. In the course of the investigation of the formation of the ferrite film, we have found that the ferrite films orient under some reaction conditions. Thus, it seemed that a study of the ferrite films would provide a knowledge for understanding the anisotropy of the crystal growth of the ferrites in aqueous solutions. On the other hand, by means of X-ray diffractometry we can not observe the direction of the crystal growth for the ferrite powders (100—200 nm), which are formed by the air-oxidation reaction of the hydroxides of Fe(II) and other metal ions.

The purpose of the present paper is to study the anisotropy of the crystal growth of the ferrite in an aqueous solution using "ferrite plating", by which the ferrite film is piled up on the glass plate in an aqueous solution. We have adopted the "thin liquid-film method" (TLF-method) for piling up the ferrite film on the glass plate. The TLF method has previously been presented by the present authors[14—16)] as a new process for piling up the ferrite films in an aqueous solution.

Experimental

Chemical. All the chemicals used were of an analytical grade. The $FeCl_2 \cdot nH_2O$ (n=3.5), $NaNO_2$, and CH_3COONH_4 were purchased from Wako Chemical Industries, Ltd. Distilled water was used for the preparation of the chemical solution.

Procedure. The reaction cell described previously was used.[14)] A cover-glass (10×10×0.15 mm^3) was used as a substrate. The cover-glass was washed with a neutral detergent and was sonicated in the solution of a neutral detergent for 3 min, followed by washing with distilled water. In each of the two beakers filled with distilled water (1 dm^3), CH_3COONH_4 (2 g) was dissolved; N_2 gas was then passed through each solution for 2 h to remove the dissolved oxygen. In one of the solutions, $FeCl_2 \cdot nH_2O$ (n=3.5) (1—4 g) was dissolved (reaction solution), while in the other solution, $NaNO_2$ (1.4 g) was dissolved (oxidizing solution). The pH values of the solutions (reaction and oxidizing solutions) used adjusted to the desired value with a 0.05 mol dm^{-3} sodium hydroxide solution. The distilled water was passed through the reaction cell until the cell temperature attained 90 °C. After it has passed through the reaction solution for about 3 min, the oxidizing solution was intermittently introduced into the cell, while the reaction solution was continuously passed through the cell. The resting time (interval) between passing through oxidizing solution and the time during the passing through of oxidizing solution were controlled using electric valves regulated with a microcomputer, NEC PC 9801-VX. After a 30-min reaction, the heating was turned off and the distilled water was passed through the reaction cell. When the cell temperature became below 50 °C, the cover-glass substrate was taken out of the cell. The surface of the cover-glass substrate turned black due to the ferrite film (Fe_3O_4, Co(II)-, and Zn(II)-ferrite) piled up on the glass-substrate. After the surface of the glass-substrate has been washed with the distilled water, the surface was dried in air at room temperature. The samples thus obtained were subjected to X-ray diffractometry (Rigaku RAD-2A). The 2θ angles of the diffraction peaks were calibrated against silicon powder using Mn-filtered Fe-K_α radiation.

Chemical Analysis. The ferrite films on the glass-substrates (2X2 mm^2), were dissolved in a 1:1 HCl solution at 70 °C. The Fe_{total} in the HCl solution was determined by the use of an atomic absorption spectrometer (Varian AA-875). The film thickness was estimated from the results of the chemical analysis based on the density of the Fe_3O_4 (=5.24).

Results and Discussion

Deposition of Fe_3O_4 Film by the "Thin Liquid-Film Method" (TLF-Metod). The X-ray diffraction analysis revealed that the deposition was a Fe_3O_4 film, scattering due to reported impurity phase not being observed under the conditions reported in this paper. Thus, by the TLF method, we can pile up the Fe_3O_4 film on the glass-substrate.

The parameters which determine the reaction conditions for the formation of the Fe_3O_4 film by the TLF method are the reaction pH, the flow rates of the reaction solution (V_f=mol min^{-1}) and the oxidizing solution (V_o=mol min^{-1}), the concentrations of the reaction solution (concentration of Fe(II) ions: C_f= mol dm^{-3}) and the oxidizing solution (C_o=mol dm^{-3}), the resting time (interval) between flowing the oxidizing solution (t_i/s), and the time during which the oxidizing solution is passed through (t_o/s). We fixed the parameters of the V_f (2.1X10^4 mol min^{-1}) and C_o (0.020 mol dm^{-3}) and studied the deposition of the Fe_3O_4 film by changing the parameters of the V_o, t_o, C_f, t_i and the reaction pH.

Anisotropy of the Crystal Growth of Fe_3O_4. Figure 1 shows the X-ray diffraction pattern of the Fe_3O_4 film piled up on the glass substrate at V_o=3.0X10^{-4} mol min^{-1}, t_i=3 s, C_f=0.021 mol dm^{-3}, t_o=3 s, and at pH=7.2. As can be seen from Fig. 1, the Fe_3O_4 grew in the (111) direction. Here, we introduce a new parameter, O_{ind} (dm min^{-1}), given by $(V_o \times t_o)/(t_i \times C_f)$. The reaction at a higher O_{ind} value is in a higher oxidation state, since the O_{ind} parameter is higher at the higher V_o and t_o values, and at the lower t_i and C_f values. We call this state the "oxidation-state". When the O_{ind} is low, the reaction is in a lower oxidation-state, which we call a "Fe^{2+}-rich state". The dimension of the O_{ind} (dm^3 min^{-1}) shows that the degree of the oxidation state is apparently related to the flow rate. The value of O_{ind} for Fig. 1 is 1.4X10^{-2} dm^3 min^{-1}. The relationship between the magnitude of O_{ind} and anisotropy will the discussed below.

Figure 2 shows the X-ray diffraction pattern of the Fe_3O_4 film oriented in the (100) direction. It should be noted that the direction of the Fe_3O_4 crystal growth varies with the reaction conditions, as is shown by Figs. 1 [(111)-orientation] and 2 [(100)-orientation]. The value of the O_{ind} for Fig. 2 is 3.38X10^{-4} dm^3 min^{-1}. From the difference between the values of O_{ind} of Figs. 1 (O_{ind}=1.4X10^{-2} dm^3 min^{-1}) and 2 (O_{ind}= 3.38X10^{-4} dm^3 min^{-1}), we can say that the Fe_3O_4 crystal grows in the (111) direction in the "oxidation state" (a higher value of O_{ind}=1.4X10^{-2} dm^3 min^{-1}), while it grows in the (100) direction in the "Fe^{2+}-rich state" (O_{ind}=3.38X10^{-4} dm^3 min^{-1}).

The Fe^{2+} ion in the inverse spinel of the Fe_3O_4 occupies the B site (octahedral site); therefore, the formation rate of the B site is lower in the "oxidation-state", since the concentration of Fe^{2+} ions is low.

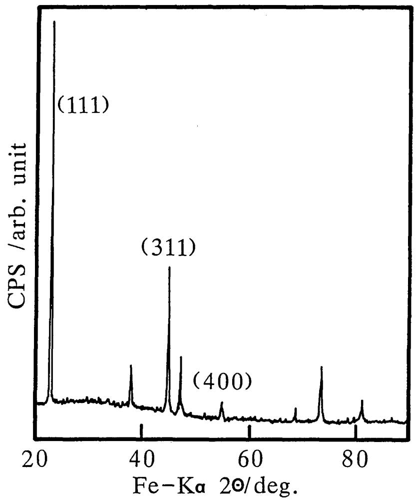

Fig. 1. The X-ray diffraction pattern of the Fe_3O_4 film deposited on the glass substrate; anisotropy in the (111) direction in "the oxidation-state". V_o= 3.0X10^{-4} mol min^{-1}, t_i=3 s, C_f=0.021 mol dm^{-3}, t_o=3 s and $(V_o \times t_o)/(t_i \times C_f)$=1.4X10^{-2} (=$O_{ind}$).

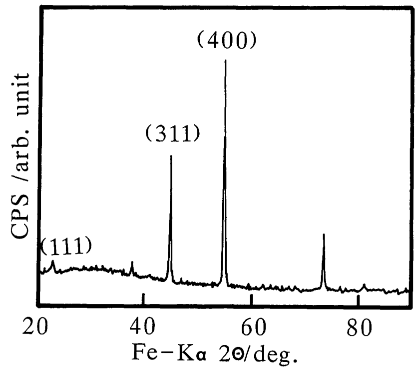

Fig. 2. The X-ray diffraction pattern of the Fe_3O_4 film deposited on the glass substrate; anisotropy in the (100) direction in "the Fe^{2+}-rich state"; V_o=4.0X10^{-4} mol min^{-1}, t_i=12 s, C_f=0.0079 mol dm^{-3}, t_o=0.8 s and $(V_o \times t_o)/(t_i \times C_f)$=3.4X10^{-4} (=$O_{ind}$).

Under such conditions, the sublattice of the A site (tetrahedral) to be occupied by Fe^{3+} (inverse spinel) ions will be preferentially constructed. This means that the growth direction is (111). Thus, the (111) direction of the crystal growth in the "oxidation-state" seems reasonable. On the contrary, the construction of the sublattice of the B site would be easier in the "Fe^{2+}-rich state", since the Fe^{2+} ions, which are to be incorporated into the B site for the inverse spinel of the Fe_3O_4, are present in the solution in the reaction cell at a high concentration. We can not give a definite reason for the orientation in the direction of (100), which seems to be caused by the preferential incorporation of Fe^{2+} ions into the B site. One reason could be the fact that the B site is readily linked in the direction of the (100) plane.

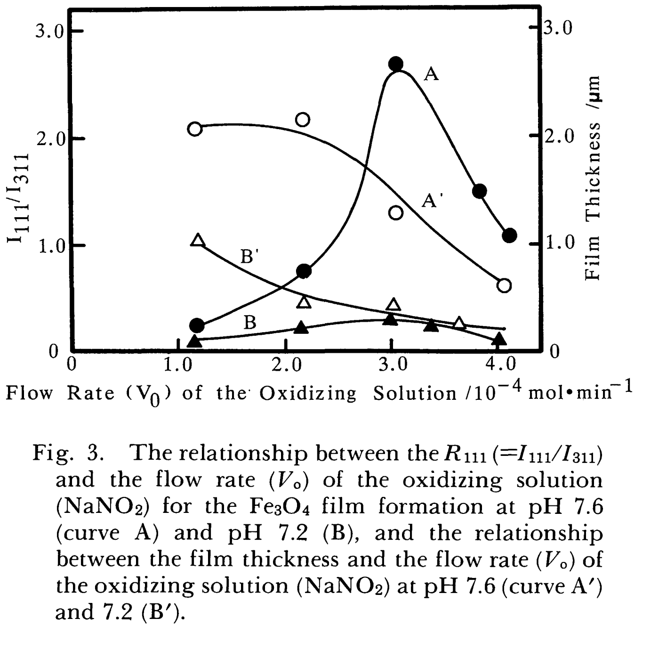

Fig. 3. The relationship between the R_{111} ($=I_{111}/I_{311}$) and the flow rate (V_o) of the oxidizing solution ($NaNO_2$) for the Fe_3O_4 film formation at pH 7.6 (curve A) and pH 7.2 (B), and the relationship between the film thickness and the flow rate (V_o) of the oxidizing solution ($NaNO_2$) at pH 7.6 (curve A′) and 7.2 (B′).

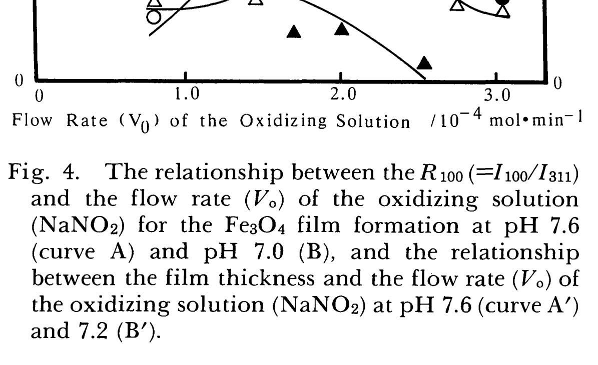

Fig. 4. The relationship between the R_{100} ($=I_{100}/I_{311}$) and the flow rate (V_o) of the oxidizing solution ($NaNO_2$) for the Fe_3O_4 film formation at pH 7.6 (curve A) and pH 7.0 (B), and the relationship between the film thickness and the flow rate (V_o) of the oxidizing solution ($NaNO_2$) at pH 7.6 (curve A′) and 7.2 (B′).

Effect of pH and Flow Rate of the Oxidizing Solution on Crystal Growth in the (111) Direction. Figure 3 shows the effect of the pH and the flow rate (V_o) of the oxidizing solution on the crystal growth in the (111) direction at $t_i=3$ s, $C_f=0.021$ mol dm^{-3} and $t_o=3$ s. The data in Fig. 3 are given by the ratio ($R_{111}=I_{111}/I_{311}$) of the peak intensities of (111) to those of (311) in the X-ray diffraction patterns. At pH 7.6 (Curve A), the R_{111} increased with an increase in the flow rate (V_o) of the oxidizing solution, attaining a maximum ($R_{111}=2.74$). However, the R_{111} decreased when the flow rate of the oxidizing solution increased further. Curve A′ in Fig. 4 shows the relationship between the film thickness and the flow rate (V_o) of the oxidizing solution at pH 7.6. As can be seen from Curves A and A′, the decrease in the R_{111} is accompanied by a decrease in the film thickness above the flow rate (V_o) of 3×10^{-4} mol min^{-1}. This suggests that some thickness is required for the anisotropy of the Fe_3O_4 crystal growth. This is also suggested by the Curves B and B′ in Fig. 3; no anisotropy was observed at any flow rate of the oxidizing solution where the films were thin, as may be seen from Curve B′.

However, as can be seen from Curves A and A′, in the range of the flow rate (V_o) of the oxidizing solution from 1.2—2.2×10^{-4} mol min^{-1} no crystal growth in the (111) direction was observed, even when thick films were obtained. When the flow rate (V_o) of the oxidizing solution increased from 2.2 to 3.1×10^{-4} mol min^{-1}, the film thickness decreased (Curve A′ in Fig. 3), indicating that the anisotropy strongly depends on the oxidation conditions. The values of the O_{ind} for Curve A in Fig. 3 are listed in Table 1, where we can see the relationship between the anisotropy R_{111} and the degree of the oxidation-state represented by the O_{ind}. We may say that the magnitude of $O_{ind}=1.45\times10^{-2}$ dm^3 min^{-1} corresponds to the "oxidation state" when the anisotropy occurs in the direction of the (111).

The lower values of the film thickness at pH 7.2 (Curve B′) are due to the lower adsorption capacity of the Fe_3O_4 film at the lower pH values. Tamaura et al.[8] reported that there is an adsorption step in the Fe_3O_4

Table 1. The Relationship between the O_{ind} and the R_{111} (pH 7.6)

Flow rate (V_o) mol min^{-1}	O_{ind} ($V_o \times t_o$)/($t_i \times C_f$) dm^3 min^{-1}	R_{111}
1.19×10^{-4}	0.570×10^{-2}	0.21
2.19×10^{-4}	1.04×10^{-2}	0.78
3.04×10^{-4}	1.45×10^{-2}	2.74
3.51×10^{-4}	1.67×10^{-2}	1.49
4.12×10^{-4}	1.96×10^{-2}	1.10

crystal growth. The adsorption of the metal ions on the surface of the iron oxides has been studied extensively studies by many workers.[17–21] Lackie et al.[17] reported that the adsorption of the metal ions proceeds more readily at a higher reaction pH; therefore, the adsorption of Fe(II) ions on the surface of the Fe_3O_4 film takes place more readily at pH 7.6 than at pH 7.2. This results in the formation of the thin film at pH 7.2.

The lowering of the growth rate of the Fe_3O_4 crystal at the higher flow rate ($V_o > 3.5\times10^{-4}$ mol min^{-1}) of the oxidizing solution (Curves A′ and B′) seems to be due to the fact that the concentration of the Fe(II) ion in the reaction solution is decreased because of the oxidation reaction occurring in the solution. The relationship between the amount of metal ions adsorbed on the surface of the metal oxides and the concentration of the metal ions in the solution is expressed by the adsorption-equilibrium equations.[17,22] Therefore, the lowering of the concentration of the Fe(II) ions in the reaction solution resulting from the oxidation reaction occurring in the solution will result in a lowering of the amount of Fe(II) ions adsorbed on the surface of the Fe_3O_4 film.

Effect of pH and Flow Rate of the Oxidizing Solution on Crystal Growth in the (100) Direction. As has been described above (Fig. 2), the anisotropy in the (100) direction occurs in the "Fe^{2+}-rich state" ($O_{ind}=3.38\times10^{-4}$ dm min^{-1}). Figure 4 shows the effect of the pH and the flow rate (V_o) of the oxidizing solution on the crystal growth of Fe_3O_4 in the (100) direction. Curves A and B in Fig. 4 show that the anisotropy ($R_{100}=I_{100}/I_{311}$) in the (100) direction occurs strongly at the flow rate of around 2.1×10^{-4} mol min^{-1} (V_o) of the oxidizing solution at pH=7.6 (Curve A′; $R_{100}=1.5$) and 7.0 (B′; $R_{100}=1.3$). The values of O_{ind} for Curves A and B in Fig. 4 are listed in Table 2. The lowering of the anisotropy (lower values of R_{100}) above 2.1×10^{-4} mol min^{-1} (V_o) is considered to be due to the decrease in the film thickness, as is shown by Curves A′ and B′.

Table 2. The Relationship between the O_{ind} and the R_{100}

	Flow rate (V_o) mol min^{-1}	O_{ind} $(V_o \times t_o)/(t_i \times C_f)$ dm^3 min^{-1}	R_{100}
pH 7.0	0.84×10^{-4}	2.55×10^{-4}	0.41
	1.45×10^{-4}	4.39×10^{-4}	0.40
	2.10×10^{-4}	6.36×10^{-4}	1.30
	2.25×10^{-4}	6.82×10^{-4}	0.83
	2.75×10^{-4}	8.33×10^{-4}	0.43
	3.38×10^{-4}	10.2×10^{-4}	0.31
pH 7.6	0.84×10^{-4}	2.55×10^{-4}	0.31
	1.75×10^{-4}	5.30×10^{-4}	0.88
	1.85×10^{-4}	5.61×10^{-4}	1.30
	2.10×10^{-4}	6.36×10^{-4}	1.52
	2.25×10^{-4}	6.82×10^{-4}	1.05
	3.38×10^{-4}	10.2×10^{-4}	0.35

As may be seen from Table 2, in the range of 0.8—1.5×10^{-4} mol min^{-1} (flow rate of the oxidizing solution; V_o), the anisotropy (R_{100}) was rather suppressed, even though thicker films were formed (Curve A′ in Fig. 4) and the condition was in the "Fe^{2+}-rich state" ($O_{ind}<1.5\times10^{-4}$ dm^3 min^{-1}; the lower value of the O_{ind} is the more "Fe^{2+}-rich state"). This indicates that the (100) anisotropy requires some degree of an oxidation state, even in the "Fe^{2+}-rich state". This means that the presence of an excess of the Fe(II) ions in the reaction solution is unfavorable for the anisotropy in the (100) direction. In the experiment of Fig. 4, the "Fe^{2+}-rich state" was generated by taking a longer interval time between introducing the oxidizing solution. The decrease in the flow rate (V_o) of the oxidizing solution results in a further increase in the Fe(II) ions reacting on the surface of the Fe_3O_4 film. The higher concentration of the Fe(II) ions on the surface of the Fe_3O_4 film would cause the dissolution of the complex of $Fe(II)_1$–$Fe(III)_2$,[10] thus resulting in the formation of the Fe_3O_4 layer via a dissolution-coprecipitation process.[10] This would be unfavorable for the orientation of the Fe_3O_4 film. Thus, the presence of an excess amount of Fe(II) ions seems to suppress the anisotropy in the crystal growth of Fe_3O_4. These considerations suggest the existence of Fe(III) ions which are not dissolved from the surface in the course of the reaction of the crystallization and which lay an important role in the orientation of the Fe_3O_4 film. This situation can be created by keeping the reaction in some degree of the oxidation-state ("meta oxidation-state"). In a slightly deviated state from the "meta oxidation-state" to an oxidation, the construction of the A site (Fe^{3+}; inverse spinel) will proceed more readily ($O_{ind}=1.5\times10^{-2}$ dm^3 min^{-1} in Table 1), since the formation rate of the B site is lower because of the lower concentration of the Fe^{2+} ions. On the contrary, in a slightly further "Fe^{2+}-rich state", the construction of the B site will proceed preferentially ($O_{ind}=3.38\times10^{-4}$ dm^3 min^{-1} in Table 2).

The anisotropy in the (100) direction was observed at pH=7.0 (Curve B in Fig. 4), where no orientation occurred in the (111) direction (Curve B in Fig. 3). This can not be explained from the difference in the film thickness, since both films are thin. It is due to the difference in the smoothness of the surface of the film. The smooth surface which was obtained for the (100) direction (Curve B in Fig. 4) is more sensitive for the observation of the orientation by means of X-ray diffractometry. This smoothness (Curve B in Fig. 4) comes from the slow deposition rate of the film (compare Curves B in Figs. 3 and 4). This slower deposition is due to the slower formation of the Fe(III) ions in "the Fe^{2+}-rich state" ($O_{ind}=0.8$—3.2×10^{-4} dm^3 min^{-1}).

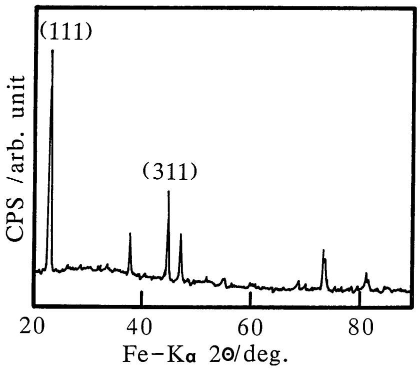

Fig. 5. The X-ray diffraction pattern of the Co(II)-ferrite film piled up on the glass substrate; anisotropy in the (111) direction in "the oxidation state." $V_o=2.25\times10^{-5}$ mol min^{-1}, $t_i=3$ s, $C_f=0.0053$ mol dm^{-3}, $t_o=3$ s and $(V_o\times t_o)/(t_i\times C_f)=4.2\times10^{-3}$ ($=O_{ind}$).

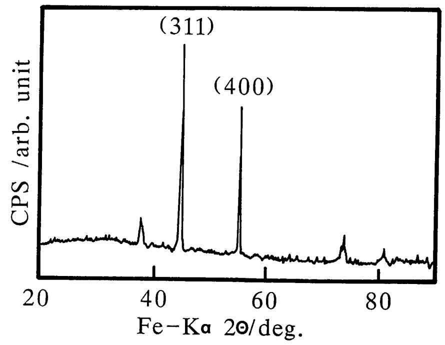

Fig. 6. The X-ray diffraction pattern of the Zn(II)-ferrite film piled up on the glass substrate; anisotropy in the (100) direction in "the oxidation state." $V_o=2.8\times10^{-4}$ mol min^{-1}, $t_i=3$ s, $C_f=5.3$ mol dm^{-3}, $t_o=3$ s and $(V_o\times t_o)/(t_i\times C_f)=5.3\times10^{-2}$ ($=O_{ind}$).

Anisotropy of the Crystal Growth of Co(II)-Ferrite film. Figure 5 shows the X-ray diffraction pattern of the Co(II)-ferrite film piled up on the glass substrate at pH 7.4 [$V_o=2.25\times10^{-5}$ mol min^{-1}, $t_i=3$ s, $C_f=0.0053$ mol dm^{-3} (the concentration of Fe(II) ions in the reaction solutions); $C_c=0.001$ mol dm^{-3} (the concentration of Co(II) ions in the reaction solution); $t_o=3$ s]. Under these conditions ($O_{ind}=4.2\times10^{-3}$ dm^3 min^{-1}), the Co(II)-ferrite film ($Co_{0.3}Fe_{2.7}O_4$) grew in the (111) direction. Although the oxidation condition was varied by changing the flow rate (V_o) of the oxidizing solution, only the (111) orientation was observed. The anisotropy (R_{111}) reached its maximum at $V_o=1.8\times10^{-4}$ mol min^{-1} ($O_{ind}=5.8\times10^{-2}$ dm^3 min^{-1}). The lower anisotropy at the lower V_o values around 1.0—1.5×10^{-4} mol min^{-1} is considered to be due to a shift toward the "Fe^{2+}-rich state" upon the lowering of the flow rate of the oxidizing solution. When we carried out the experiment under the same conditions as those of Fig. 2 (in the "Fe^{2+}-rich state"), no orientation was observed. Thus, it was found that the Co(II)-ferrite grew only in the (111) direction in the "oxidation-state" ($O_{ind}=5.8\times10^{-2}$ dm^3 min^{-1}).

Anisotropy of the Crystal Growth of Zn(II)-Ferrite film. Figure 6 shows the X-ray diffraction pattern of the Zn(II)-ferrite film piled up at pH 7.6 [$V_o=2.8\times10^{-4}$ mol min^{-1}, $t_i=3$ s, $C_f=5.3\times10^{-3}$ mol dm^{-3} (the concentrations of Fe(II) ions in the reaction solution); $C_z=6.15\times10^{-3}$ mol dm^{-3} (the concentrations of Zn(II) ions in the reaction solution); $t_o=3$ s]. Under these conditions the Zn(II)-ferrite film ($Zn_{0.8}Fe_{2.2}O_4$) grew in the (100) direction ($O_{ind}=5.3\times10^{-2}$ dm^3 min^{-1}). A maximum orientation was observed at $V_o=3\times10^{-4}$ mol min^{-1} ($O_{ind}=5.5\times10^{-2}$ dm^3 min^{-1}).

The values of the O_{ind} where R_{111}(Co(II)-ferrite) and R_{100}(Zn(II)-ferrite) reaches there maximum were 5.8×10^{-2} and 5.5×10^{-2} dm^3 min^{-1}, respectively. These values indicates that the reaction is in the "oxidation-state" for the orientation of the Co(II)- and Zn(II)-ferrite films. It is interesting that, although the reaction conditions are the same (both are in the "oxidation-state"; $O_{ind}=5.5$—5.8×10^{-2} dm^3 min^{-1}), the anisotropy of the crystal growth is different between Co^{2+} [the (111) direction] and Zn^{2+} [the (100) direction]. This seems to come from the site preference of the metal ions; Co(II)-ferrite is inverse spinel (A site; Fe^{3+}) and Zn(II)-ferrite, normal spinel (A site; Zn^{2+}). In the "oxidation-state", the Fe^{3+} ions are formed at a higher rate than in the "Fe^{2+}-rich state". This will result in the acceleration of the construction of the B site for the normal spinel, since the Fe^{3+} ions are preferentially incorporated into the B site (normal spinel), and the Zn^{2+} ions, into the A site (normal spinel).

On the other hand, the anisotropy in the (111) direction is considered to take place when the reaction deviates slightly toward the "oxidation-state" from the "meta-oxidation state". Since the Co(II)-ferrite is the inverse spinel, one of the two Fe^{3+} ions is preferentially incorporated into the A site, and the other into the B site. Under the "oxidation-state ($O_{ind}=5.8\times10^{-2}$ dm^3 min^{-1})", the Fe^{3+} ions are formed at a higher rate; therefore, the incorporation reaction of the Fe^{3+} ions will be accelerated. This means that the rate of the construction of the B site with the Fe^{3+} and Co^{2+} ions, which are preferentially incorporated into the B site (Co(II)-ferrite is inverse spinel), is lowered. This will result in the anisotropy in the direction of the (111).

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