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Preparation of spinel-type ferrite thin films by the dip-coating process and their magnetic properties

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Films of spinel-type ferrite, MFe_2O_4 (M = Ni, Co, Mg, $Li_{0.5}Fe_{0.5}$) have been prepared by a dip-coating method from the sol–gel process. Ferric nitrate, nickel nitrate, cobalt nitrate and lithium nitrate were used as raw materials, and glycerol and formamide were used as solvents. A film was prepared by dipping a silica glass plate. The spinel-type ferrite was obtained by heat-treatment at 700–900 °C for 2 h in air. The film thickness was about 0.8 μm. The saturation magnetization, σ_r, of the film and powder with composition $50NiO \cdot 50Fe_2O_3$ was 196 emu cm^{-3} and 29.1 emu g^{-1}, respectively, and the coercive force, H_c, was 140 and 95 Oe, respectively, after heat-treatment at 800 °C for 2 h. In particular, the films were shown to have a much larger H_c than the powder. The grain growth of spinel ferrite may be subject to restriction because it is in progress above an amorphous base-plate. The crystals are therefore aligned with the base-plate and have uniaxial anisotropy.

1. Introduction

Spinel-type ferrite, the chemical formula of which is MFe_2O_4 (M = Ni, Co, Mg, $Li_{0.5}Fe_{0.5}$), is a soft ferrite material used in transformers, magnet cores of coils, switching sources, recording magnetic heads and memory elements. The methods now used for preparing magnetic films, such as the vacuum evaporation method, sputtering method, and chemical vapour deposition (CVD) method are not suitable for preparing large specimens and controlling the composition. On the other hand, the dip-coating method from the sol–gel process [1] is a very simple film-synthesizing method in which a specified substrate is dipped in a uniform solution (sol), withdrawn from the solution, dried and heat-treated. With this method, films with a uniform composition can be obtained even in multi-component systems since the materials are mixed in the solution state, and a coating can be applied to large and intricately shaped objects. Although many types of functional film with various electrical [2, 3], optical [4, 5] and mechanical properties [6] have been obtained by this method, there are almost no reports on films with magnetic properties. In the present study, thin films and powders containing spinel-type ferrite MFe_2O_4 (M = Ni, Co, Mg, $Li_{0.5}Fe_{0.5}$) crystals were prepared, and the optimum preparation conditions and the magnetic properties of the film and powder obtained were investigated.

2. Experimental procedure

2.1. Preparation of specimens

Fig. 1 shows the flow-chart for preparation of films and powder from the sol–gel process. The compositions investigated were $50MO \cdot 50Fe_2O_3$, and $60MO \cdot 40Fe_2O_3$ (M = Ni, Co, Mg, $Li_{0.5}Fe_{0.5}$). Iron nitrate, nickel nitrate, cobalt nitrate and lithium nitrate were used as raw materials. Glycerol, formamide and HCl were used as solvents. The nitrates of various metal were taken in accordance with the above composition. H_2O, 3 N HCl, glycerol and formamide were added. These were stirred and dissolved to form a coating solution. Transparent silica glass was used as a base-plate. The plate was dipped into the above-mentioned solution and withdrawn at a rate of about 0.2 cm s^{-1} so that a film was formed on the plate. The film was dried at 80 °C for 2 h and successively heated to 200 °C at a rate of 2 °C min^{-1}, and heat-treated for 2 h to form a ferrite film. Drying and heat-treatment were performed in air. For comparison, the powder was obtained by grinding in a mortar after the coating solution had dried, and was heat-treated under the same conditions as for the thin film.

2.2. Analysis

An X-ray diffractometer (Rigaku model CN2013) was used to identify the crystalline phases of the powder

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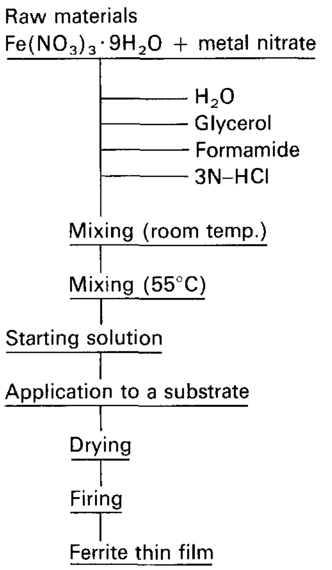

Figure 1 Preparation procedure of spinel-type ferrite thin films.

samples. The crystalline phases of thin-film samples were identified by using a Rigaku Model CN4148 with a thin-film attachment and carbon monochromator. FeK_α was used as a target in both cases. Thin film thicknesses were measured using a Model ET-10S high-precision thin-film height difference meter from Kosaka. Magnetic properties were measured using a Model BHV-55VSM vibrating sample type magnetization meter (VSM) from Riken Electronics; coercive force (H_c), saturation magnetization (σ_s), and residual magnetization (σ_r) were measured from the hysteresis loops of thin film and powder samples at room temperature. An i.r. spectrometer (Shimazu type IR-440) was used for analysing the evaporation of solvent, burning conditions and crystallization of the drying powder. An instrument for thermogravimetry (TG) and differential thermal analysis (DTA) (Rigaku type 8078) was used for analysing the structure by heat-treatment of the drying powder. An atomic absorption spectrometer (Shimazu AA-670G) was used for analysing the composition ratio of Ba and Fe of the films and drying powder.

3. Result and discussion

3.1. Preparation of films

In this study, inorganic materials as each nitrate were used as raw materials. The following steps were considered to occur when forming a thin film by sintering an inorganic salt dissolved in an organic solvent and deposited over a substrate:

1. An inorganic salt was dissolved in an organic solvent, to form a uniform solution.
2. A metallic atom interacted with an oxygen atom during the hydrolysis, polymerization–condensation and sintering processes, to make the metallic atoms bond to each other via oxygen atoms.
3. The solvent was removed from the film by vaporization, oxidation and decomposition, making metal–oxygen bonding stronger.

The experiments were carried out while taking into consideration the above three steps. Ferric nitrate was used as a raw material and similarly the nitrate was used for other raw materials. All these materials dissolved well in all the solvents used in this study. For the solvent, lower alcohols such as ethanol and methanol were found inadequate, because it was difficult to spread the solution over the substrate uniformly, though they dissolved well in the solvent. The use of glycerol, a high boiling-point solvent, allowed the solution to adhere to the base plate. It was found, however, that glycerol, which is very viscous, caused the film to become powdery. To reduce the viscosity, therefore, water and formamide were added to obtain a thin film without cracks. The thin film obtained after heat-treatment did not peel off when dipped in 3 N HCl or 3 N NaOH for several hours. The thin film was so strong that it was not peeled off by mechanical friction. A film thickness of about 0.08 μm was obtained by one dip-coating.

3.2. Determination of crystallization conditions

Fig. 2 shows the powder X-ray diffraction patterns of the composition $50ZnO \cdot 50Fe_2O_3$ for different heat-treatment conditions. α-Fe_2O_3 was only obtained for heat-treatment at 900 °C for 2 h immediately after the drying of the powder (Fig. 2a); the powder heat-treated at 400 °C was amorphous from X-ray diffraction. Successive heat-treatment at 900 °C for 2 h

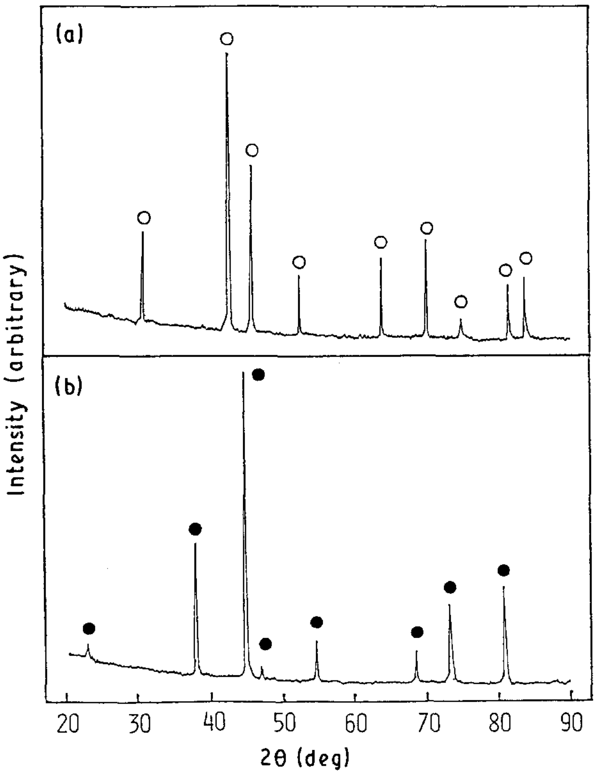

Figure 2 Powder X-ray diffraction patterns (FeK_α) of $50ZnO \cdot 50Fe_2O_3$: (a) heat-treated at 900 °C for 2 h after drying at 200 °C for 12 h, (b) heat-treated at 400 °C for 2 h and 900 °C for 2 h after drying at 200 °C for 12 h. (○) α-Fe_2O_3, (●) $ZnFe_2O_4$.

produced only a single phase of Zn ferrite. Figs 3 and 4 show the powder X-ray diffraction patterns of the compositions $50NiO \cdot 50Fe_2O_3$ and $50CoO \cdot 50Fe_2O_3$ heat-treated at various temperatures for 2 h. The peaks of spinel-type ferrite were found on heat-treatment at 400 °C for 2 h, and the crystallinity increased with increasing heat-treatment temperature.

α-Fe_2O_3 was observed for the mixture with chemical stoichiometry components Mg and Li ferrite. The reason was considered to be the vaporization of the relatively light elements Mg and Li in the calcination. Fig. 5 shows effects of the composition ratio and the raw material on Li ferrite. The Li ferrite single phase was obtained by the use of Li nitrate in the composition $60Li_2O \cdot 40Fe_2O_3$.

Fig. 6 shows DTA and TG results for the drying powder with composition $50CoO \cdot 50Fe_2O_3$. Evaporation and oxidation started at approximately 300 °C, and disappearance of the solvent component was observed over a fairly wide temperature range up to about 370 °C. Of the solvents tested in this study, glycerol was found to give the best film. Based on extensive investigations, it was decided that the optimum combination was iron nitrate as the Fe source, other nitrates, and glycerol as the solvent. The major solution properties required for producing a good film are adequate viscosity and boiling point. Another important property affecting film quality is

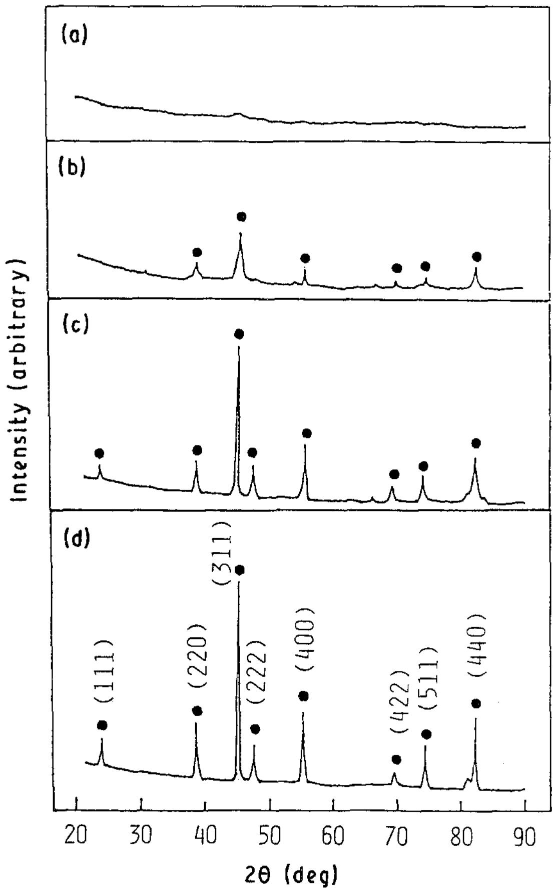

Figure 3 Powder X-ray diffraction patterns (FeK_α) of $50NiO \cdot 50Fe_2O_3$ heat-treated at various temperatures for 2 h after drying at 200 °C: (a) 200 °C dry, (b) 400 °C, (c) 500 °C, (d) 700 °C. (●) $NiFe_2O_4$.

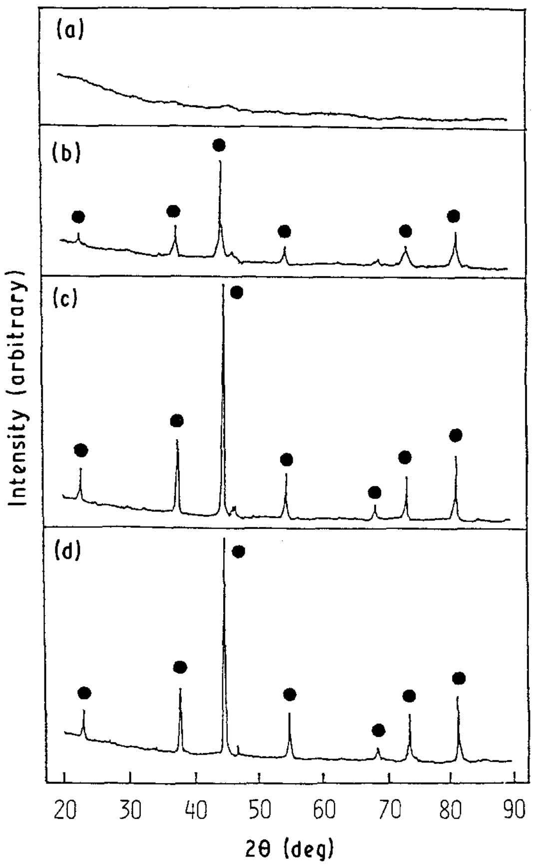

Figure 4 Powder X-ray diffraction patterns (FeK_α) of $50CoO \cdot 50Fe_2O_3$ heat-treated at various temperatures for 2 h after drying at 200 °C: (a) 200 °C dry, (b) 400 °C, (c) 700 °C, (d) 800 °C. (●) $CoFe_2O_4$.

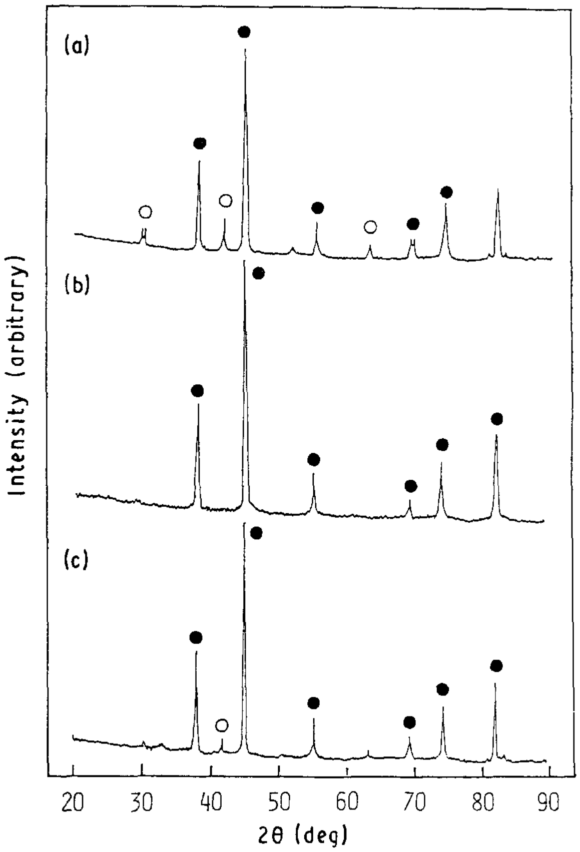

Figure 5 Powder X-ray diffraction patterns of heat-treated products with the following components (700 °C, 2 h): (a) 50 $(Li_{0.5}Fe_{0.5})O \cdot 50Fe_2O_3$, raw material $LiNO_3$; (b) 60 $(Li_{0.5}Fe_{0.5})O \cdot 40Fe_2O_3$, raw material $LiNO_3$; (c) 60 $(Li_{0.5}Fe_{0.5})O \cdot 40Fe_2O_3$, raw material LiCl. (●) $Li_{0.5}$ $Fe_{2.5}O_4$, (○) α-Fe_2O_3.

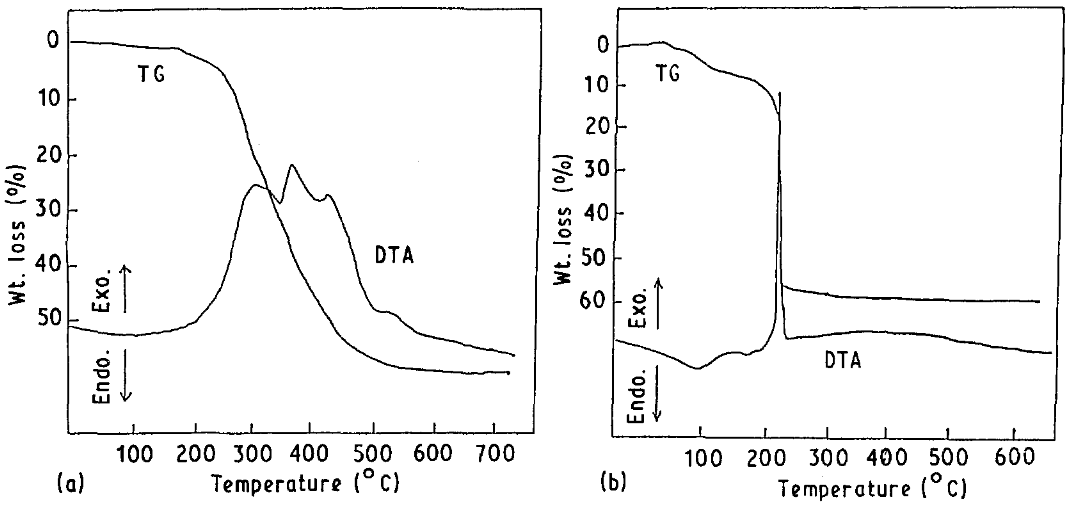

Figure 6 DTA and TG curves of $CoFe_2O_4$ dried powder: (a) solution: glycerol, dried at 200 °C for 12 h, (b) solution: ethanol, dried at 100 °C for 12 h.

the solvent evaporation rate during the drying process. These were considered to favourably affect film formation and repeatability.

Fig. 7 shows the i.r. absorption spectra for each heat-treatment temperature for the composition $50NiO \cdot 50Fe_2O_3$. The absorption of glycerol was observed for the drying sample. The –OH group peak of the solvent was observed at 3300 cm^{-1} for heat-treatment at 400 °C, but its peak disappeared above 500 °C. On the other hand, two absorption peaks were observed at 400 and 800 cm^{-1} for heat-treatment above 400 °C. These peaks were considered to be due to the stretching vibration of Fe^{3+}–O^{2-} with co-ordination number 4 or 6 [7]. The spinel ferrite lattice was formed by heat-treatment above 400 °C and this result agreed with the powder X-ray diffraction patterns. Spinel-type ferrites are cubic-lattice crystals and the spacing is as follows [8]:

$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \tag{1}$$

where a is the lattice constant of spinel-type ferrite. Table I shows the results determined using Equation 1 for the lattice constant of each spinel ferrite. The measured values agreed with the reference data.

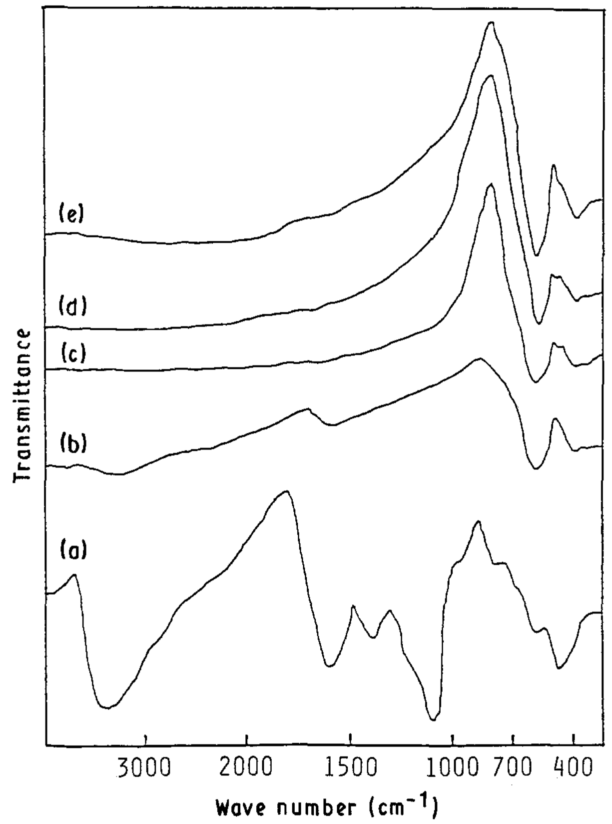

Figure 7 I.r. spectra of $50NiO \cdot 50Fe_2O_3$ powder heat-treated at various temperatures for 2 h after drying at 200 °C: (a) 200 °C dry, (b) 400 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C.

3.3. Magnetic properties

Fig. 8 shows the hysteresis loops of the powder and the thin film. By applying a magnetic field of 2.5 kOe with a VSM, the hysteresis loops of thin film and powder were measured at room temperature, from which the coercive force (H_c), saturation magnetization (σ_s) and residual magnetization (σ_r) were determined. The unit of magnetization (σ) was expressed in magnetization per unit volume (unit: emu cm^{-3}) for thin films, and in magnetization per unit weight (unit: emu g^{-1}) for powders. Table II lists the magnetic properties of thin films and powders heat-treated at 700 °C for 2 h.

TABLE I Lattice constants of spinel ferrite

Composition	Lattice constant (nm)	
	Measured	Literature [9, 10]
$NiFe_2O_4$	0.8329	0.833
$CoFe_2O_4$	0.8395	0.838
$MgFe_2O_4$	0.8393	0.837
$Li_{0.5}Fe_{2.5}O_4$	0.8335	0.833
$ZnFe_2O_4$	0.8432	0.8433

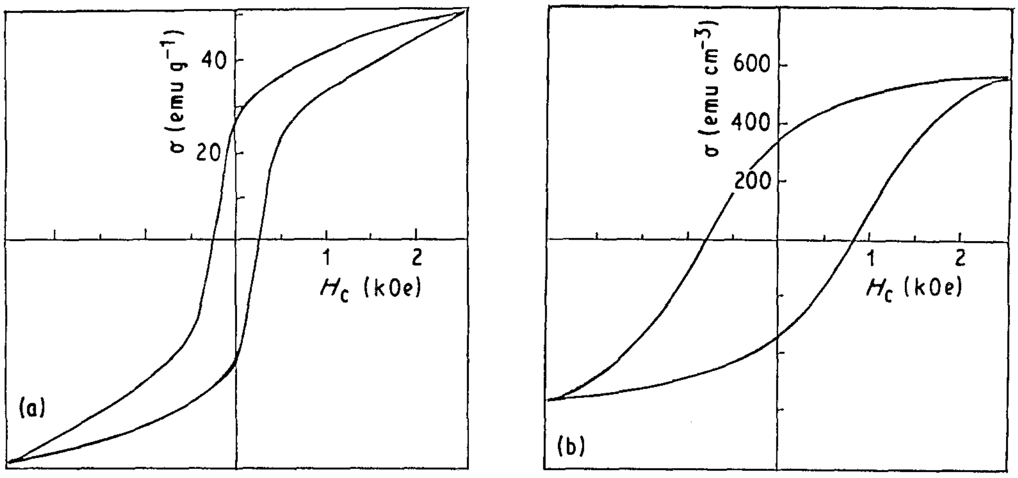

Figure 8 Magnetic hysteresis loops of 50CoO · 50Fe_2O_3 heat-treated at 700 °C for 2 h after drying at 200 °C: (a) powder, (b) film.

TABLE II Magnetic properties of spinel-type ferrite films and powder heat-treated at 700 °C for 2 h after drying at 200 °C for 12 h

Composition	Film			Powder		
	H_c (Oe)	σ_s (emu cm^{-3})	σ_r (emu cm^{-3})	H_c (Oe)	σ_s (emu g^{-1})	σ_r (emu g^{-1})
50NiO·50Fe_2O_3	140	196	34.0	95	29.1	66.02
50CoO·50Fe_2O_3	810	557	347	575	50.1	28.3
50MgO·50Fe_2O_3	75	277	109	16	20.0	6.14
60($Li_{0.5}Fe_{0.5}$)O·40Fe_2O_3	170	719	277	8	49.5	14.6

The magnetic properties from solid-phase reaction of NiO and α-Fe_2O_3 powders showed $H_c = 155$ Oe and $\sigma_s = 29.0$ emu g^{-1} after heat-treatment at 900 °C for 1 h. The value of σ_s from solid-phase reaction heat-treated at 900 °C showed almost the same value as σ_s from the sol–gel process. The sintering of the powder from the sol–gel process was possible at low temperature compared with those for a specimen using solid state reaction. The thin films prepared in these experiments had a higher coercive force than the powders. The grain growth of spinel ferrite may be subject to restriction because it is in progress above an amorphous base-plate. The crystals are therefore aligned with the base-plate and have uniaxial anisotropy. H_c for Co ferrite thin films had a higher coercive force than other types of ferrite thin film. The reason for this will be considered as follows. The energy of crystal magnetic anisotropy for a cubic lattice is according to the formula

$$E_a = k_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + k_2\alpha_1^2\alpha_2^2\alpha_3^2 \quad (2)$$

where $\alpha_1, \alpha_2, \alpha_3$ are direction parameters of the crystal axes; k_1 and k_2 are crystal magnetic anisotropy constants. In general, k_1 show a negative value for spinel ferrite. This result means that the magnetization easy axis shows four directions of (1 1 1), (1 1 $\bar{1}$), (1 $\bar{1}$ 1) and ($\bar{1}$ 1 1). The k_1 value of Co ferrite shows a larger value (about twice that of those of other ferrites) because the Co^{2+} ion in Co ferrite occupies an octahedron. This result shows that the magnetization easy axis direction has three directions of (1 0 0), (0 1 0) and (0 0 1). Co ferrite therefore shows a larger magnetic anisotropy and the coercive force shows a larger value than those of other ferrites with the same magnetic anisotropy.

Figs 9 and 10 show the magnetic properties for each heat-treatment temperature of Co ferrite and Li ferrite

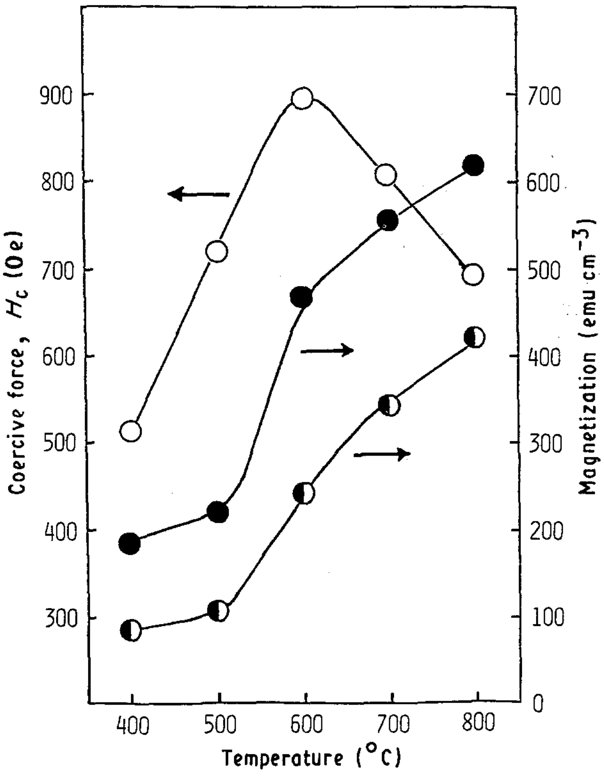

Figure 9 Magnetic properties of $CoFe_2O_4$ films heat-treated at various temperatures for 2 h after drying at 200 °C: (○) H_c, (●) σ_s, (◑) σ_r.

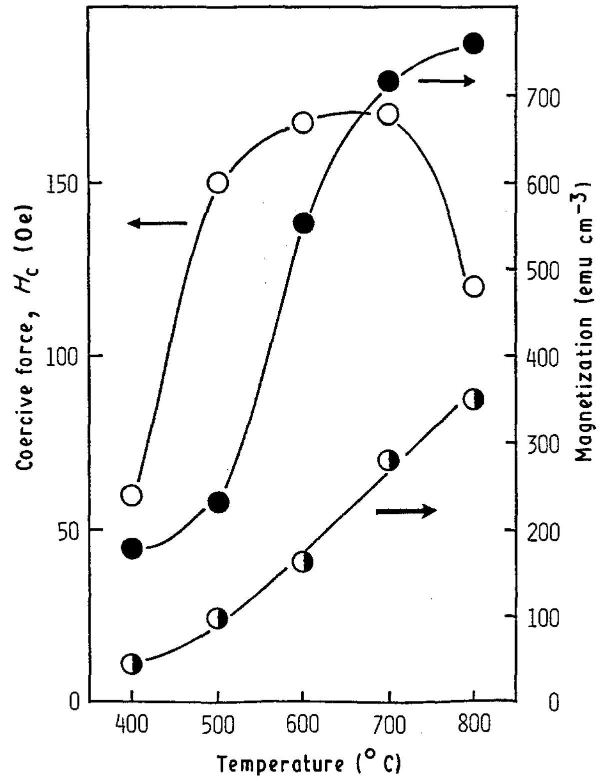

Figure 10 Magnetic properties of $Li_{0.5}Fe_{2.5}O_4$ films heat-treated at various temperatures for 2 h after drying at 200 °C: (○) H_c, (●) σ_s, (◑) σ_r.

films. The coercive force showed a maximum value at 600 °C with both ferrites. These results were considered to indicate the formation of a single magnetic domain for 600 °C heat-treatment temperature. On the other hand, the saturation magnetization and residual magnetization increased with increasing heat-treatment temperature. These results are related to a rise in the crystallinity.

Fig. 11 shows the relation of the coercive force and grain size according to Cullity [11]. The coercive force shows a maximum in the single magnetic domain region. This result shows a relation similar to the experimental results.

4. Conclusions

The following conclusions were reached about the preparation of spinel-type ferrite films by the dip-coating method.

1. A uniform thin film was prepared by using various metal nitrates as raw materials and glycerol as a solvent.

2. The crystalline phase of spinel-type ferrite appeared in material prepared by heat-treatment at 400 °C, and the crystallinity increased with increasing heat-treatment temperature.

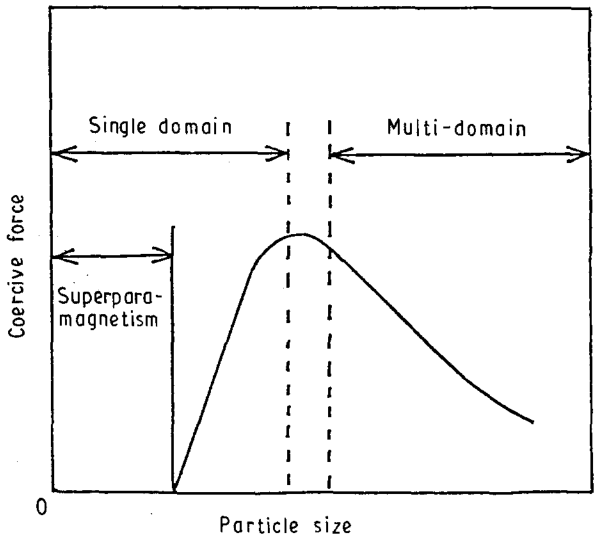

Figure 11 Relationship of coercive force and particle size.

3. The coercive force increased with increasing heat-treatment temperature and reached a maximum in the range of temperature from 600 to 700 °C, and then decreased with increasing temperature. The reason was considered to be that the films of spinel-type ferrite showed a single magnetic domain structure after heat-treatment at 600 to 700 °C.

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