Ceramics International **21** (1995) 21–27

Preparation of Cobalt Doped Nickel Ferrite Thin Films on Optical Fibers by Dip-Coating Technique

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(Received 27 April 1994; accepted 2 September 1994)

Abstract: Cobalt doped $NiFe_2O_4$ thin films were synthesized using dip-coating wet-chemical process using a solution of iron (III) nitrate dissolved in ethylene glycol and 2-methoxyethanol. Films coated on flat (alumina plates, fused silica, slide glass) substrates and optical fibers were dense and without defects. The onset of the film crystallization was between 450 and 500°C and crystallinity increased with increasing processing temperature. Magnetization of ferrite films on optical fibers was nearly reversible in external magnetic field H_{ext} up to about 2·4 kA/m even without preceding AC demagnetization. The magnetization of 255×10^{-3}T for $Ni_{0.99}Co_{0.01}Fe_2O_4$ films processed at 750°C for 2 h was observed. No further improvement in magnetic properties was found beyond this temperature.

1 INTRODUCTION

Spinel type magnetic thin films prepared by a number of methods (sputtering, OMCVD, ferrite plating, etc.) are of widespread interest due to their many applications in microelectronics and their use for magneto-optic devices.[1–4] From possible convenient deposition methods, a sol–gel method has several advantages because of their comparatively low processing temperatures, low cost, and capability of preparing materials with very good homogeneity.[5] Additionally, a dip-coating technique is capable of fabricating films even on an extremely complex shaped substrate. However, there is only a small number of data on iron based sol–gel films[6–11] and to our knowledge little was done in the characterization of nickel ferrite sol–gel films.[7]

Spinel type oxides with appropriate doping (several compositions of A_{1-x} B_x Fe_2O_4, where A, B are transition elements such as Ni, Co, Fe, Mn, Zn and Cu) may possess a high magnetostrictive constant[12,13] comparable to ferromagnetic metal films. Conclusively, when a magnetic film is properly applied on a single mode optical fiber, such a device may be used as a fiber optic magnetic field sensor. Experimental evidence verifying the magnetic field characteristics of optical fibers jacketed with metallic materials was already reported.[14,15] Nickel ferrite bulk materials with low cobalt doping levels (especially 2·8 mol% Co) were reported to possess high magnetostrictive properties.[16]

An objective of this study was to characterize cobalt doped nickel ferrite thin films prepared by a wet chemical method on both flat substrates and optical fibers. As optical fibers possess an extreme curvature and are susceptible to break upon handling, some difficulties during the preparation may be expected. We previously showed[17] that film thickness is strongly dependent on a geometry (curvature) and that a film deposited on an optical fiber is several times thinner compared to that on an even plate. Taking into account the difficulty of crystallizing films on an amorphous substrate and the susceptibility of the fiber to disintegrate when thermally treated, the overall process may be relatively troublesome. For comparison, we prepared films on both amorphous (fused silica) and crystalline (alumina) flat substrates.

2 EXPERIMENTAL

Iron (III) nitrate [$Fe(NO_3)_3.9H_2O$], nickel nitrate $Ni(NO_3)_3 . 6H_2O$, and cobalt nitrate $Co(NO_3)_2 . 6H_2O$ were used as precursor materials (all purchased from Aldrich Co., ACS grade). Nitrates were chosen because of their convenience, lower expense, and easier handling compared to metal alkoxides. Interestingly, iron (III) nitrate is known to exhibit a sol–gel reaction when reacted with ethylene glycol at elevated temperature.[8–10]

Iron (III) nitrate was dissolved in ethylene glycol (heating temperature held at 70°C) in the proportion of 0·5 g of iron nitrate to 1 ml of ethylene glycol and, after cooling, mixed in an ultrasonic cleaner. The proper amounts of nickel and cobalt nitrates were dissolved in preheated 2-methoxyethanol (2-MOE) and mixed together with the iron nitrate solution while shaking. Finally the mixture of ethylene glycol, 2-MOE and polyethylene glycol (or PEG, molecular weight = 400 g/mol) was added while stirring to adjust the sol viscosity, concentration and surface tension. Substrates were boiled in the mixture of detergent and distilled water and thoroughly rinsed by water (D.I.) and ethanol. Optical fibers were left to soak in the organic solvent to remove a polymer coating. To remove all organic contaminants, the substrates were preheated to 400°C in a tubular furnace. The film thickness was controlled by the sol parameters and withdrawal speed (5—10 cm/min for plates and 60 cm/min for optical fibers). The films were then dried in air at 120°C for 3 min to promote the gelation, followed by slow heating (20°C/min) to the firing temperature (500°C). After the film thickness was built up as required (0·5–3 μm) by a multiple coating, films were annealed at temperatures ranging from 600 to 900°C. Optical fibers were put directly into a preheated furnace and usually 40–50 coating cycles were used to build up the thicknesses of 2–3 μm. Deposition of thicker films made the process time-consuming and cost ineffective.

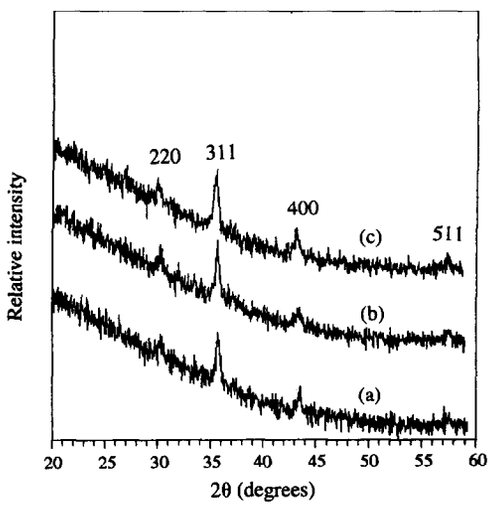

Fig. 1. XRD pattern of thin $Ni_{1-x}Co_xFe_2O_4$ film on SiO_2 processed at 600°C in air for 30 min: (a) x = 0·02, (b) x = 0·04, (c) x = 0·10.

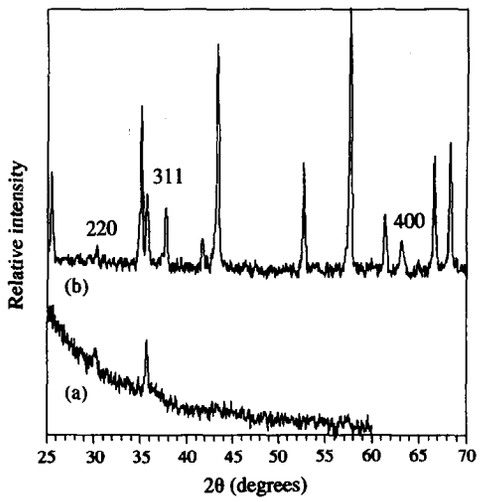

Fig. 2. XRD pattern of thin $Ni_{0.99}Co_{0.01}Fe_2O_4$ film processed at 900°C in air for 1 h on (a) fused silica, (b) alumina.

The crystallographic structure of the films was examined using a Rigaku Miniflex X-ray diffractometer with Cu K_α radiation and a film microstructure was investigated by Scanning Electron Microscopy (SEM). Magnetic properties were examined using a vibrating sample magnetometer PAR 155 at room temperature. Film thicknesses were determined by a surface roughness tester (Surfometer SF 200) or from the cross section (SEM).

3 RESULTS AND DISCUSSION

3.1 Effect of the composition and substrate on the film microstructure

The onset of the film crystallization was found at approximately 500°C. X-ray diffraction patterns

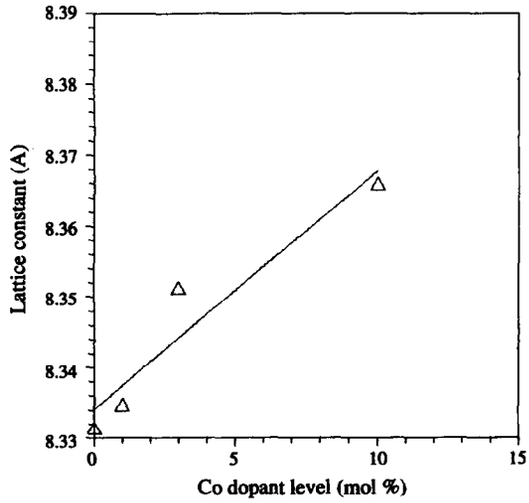

Fig. 3. The lattice constant of ferrite films as a function of cobalt content.

of cobalt doped $NiFe_2O_4$ spinel films deposited on fused silica treated at 600°C for 30 min (Fig. 1) were diffuse and less discernible. This fact is probably due to the inhibition of the crystal growth at lower temperatures on such a substrate and films were markedly less crystallized. On the other hand, a difference between the peak width of films on fused silica and those on alumina when treated at higher temperatures (900°C, 1 h), was not as pronounced (Fig. 2). This fact indicates that a crystallization barrier for films on fused silica was somewhat lowered with increasing holding temperature. Unfortunately, a temperature of 650°C did seem to be the upper limit for processing of optical fibers, otherwise fiber breaking became more frequent.

A lattice constant of cobalt doped ferrite films was determined using *d*-spacing of the {311} line from Fig. 1. With the increasing cobalt content, the lattice constant gradually increased and reached the value $a = 8{\cdot}365$ for films with 10% cobalt (Fig. 3).

Although ferrite films were in general dense and without cracks, films on fused silica were more susceptible to cracking. The microstructure of films changed with cobalt doping. Films with 3% cobalt exhibited smaller grain size [SEM micrograph in Fig. 4(a)] compared to those without cobalt [Fig. 4(b)]. A more detailed microstructural view of $Ni_{0{\cdot}97}Co_{0{\cdot}01}Fe_2O_4$ films annealed at 620°C for 1 h on glass revealed [Fig. 4(c)] low porosity and comparatively small grain size. Figure 4(d)

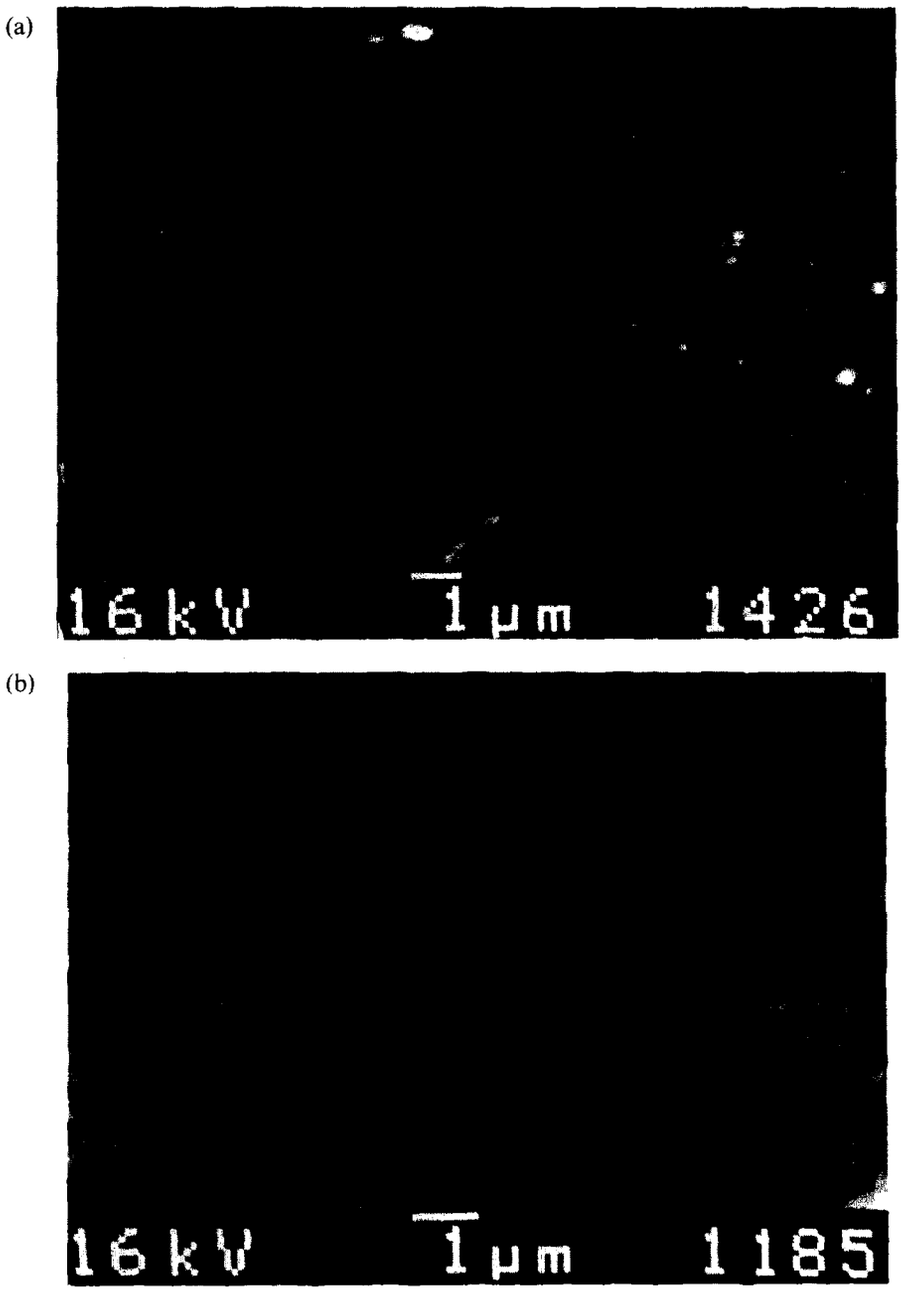

Fig. 4. SEM micrographs of $Ni_{1-x}Co_xFe_2O_4$ thin films (a) $x = 0{\cdot}03$, 600°C, 1 h, slide glass; (b) $x = 0$, 600°C, 1 h, slide glass; (c) $x = 0{\cdot}03$, 620°C, 1 h, slide glass; (d) part of cross section of the film with 1% of Co on an optical fiber (diam. = 300 μm).

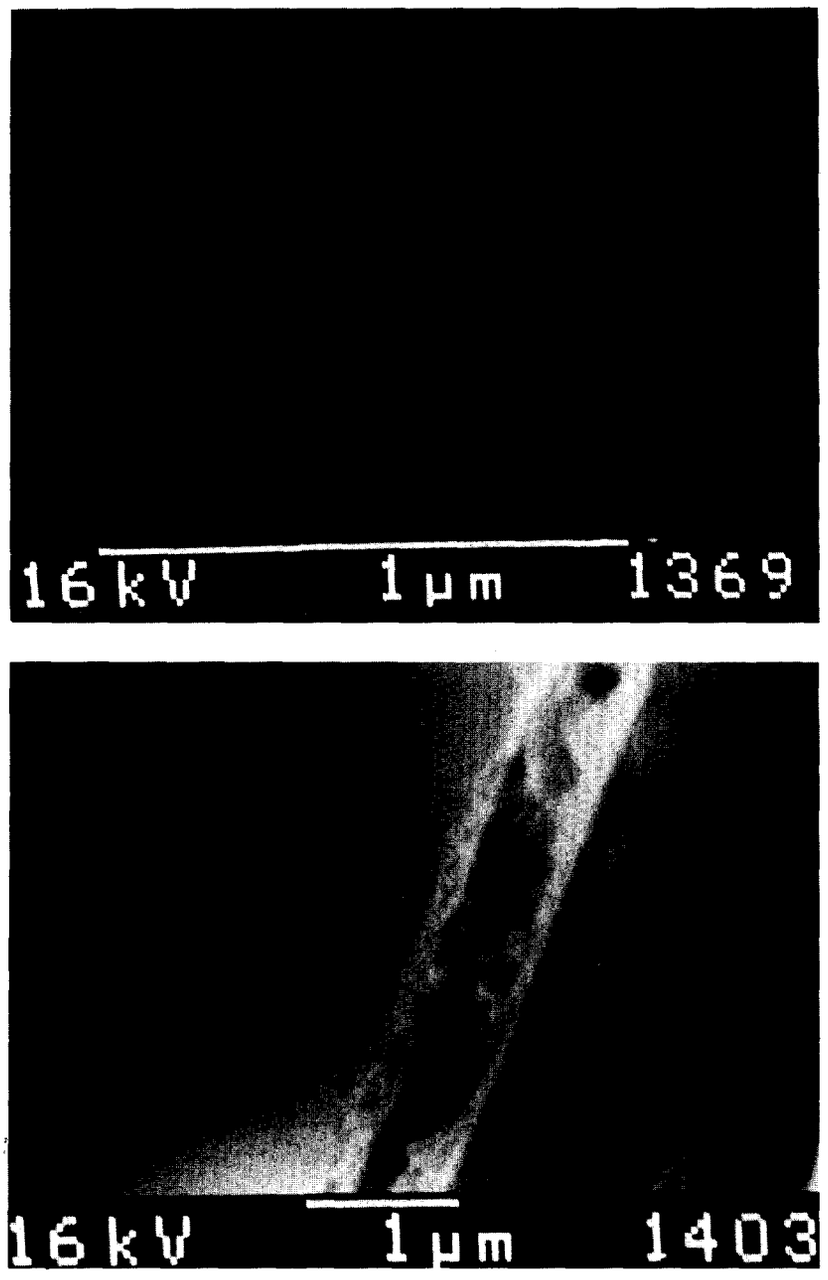

Fig. 4.—*Contd.*

shows a cross section of the film with 1% Co on an optical fiber (diam = 300 μm). No excessive residual porosity was found throughout the film and the film was uniform along the fiber circumference.

3.2 Magnetic properties of films

To evaluate values of magnetization, the volume of films was calculated using the film thickness and the specimen surface. This approach did not take into account the film density and therefore the magnetizations obtained may be rather underestimated. However, based on SEM measurements which disclosed low film porosity, we believe that calculated magnetizations are realistic. To compare the level of magnetic ordering of various samples, we evaluated magnetization at a magnetic field of 800 kA/m, which was close to the saturation value. We also evaluated coercive force H_c, defined as a half-width of magnetic hysteresis loop (MHL) at $M = 0$, and the slope of MHL $\chi_{MHL} = dM/dH$ at $M = 0$. For possible applications of thin films in magneto-optic components, a high magnetic response to relatively low magnetic fields is desired. Therefore, we also measured minor magnetic hysteresis loops (MMHL) at a small external field intensity H_{ext} to compare coercive force H_{cm} and initial susceptibility χ_{MMHL} on MMHL with values H_c and χ_{MHL} obtained from MHL. A sample was carefully demagnetized in an AC magnetic field with the amplitude decreasing to zero before each MMHL measurement. All flat samples were measured perpendicular to the film plane. MHL of optical fibers were taken using two

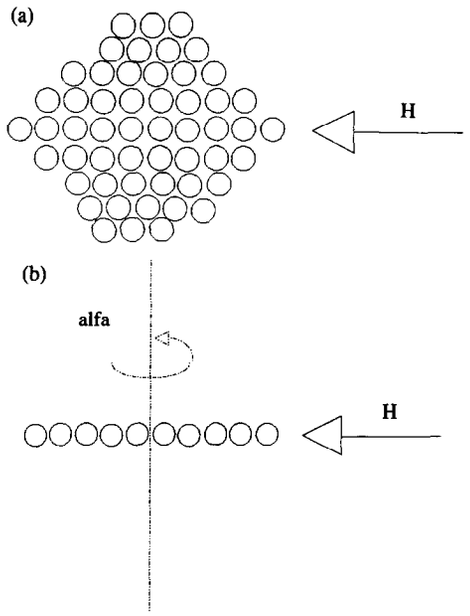

Fig. 5. Two different arrangements of optical fibers for the measurement of MHL: (a) bundle, (b) column of fibers, α is the angle with respect to magnetic field direction.

different arrangements, where a bundle [Fig. 5(a)] or column of fibers [Fig. 5(b)] was used. The bundle of approximately 30 optical fibers 0·5 cm in length must have been used to improve the measured signal.

3.2.1 MHL data taken on flat substrates

Table 1 summarizes the magnetization values for samples prepared under various conditions and of several film compositions. With increasing annealing temperature, the magnetization of films having 1% cobalt reached its maximum 265 × 10^{-3} T at a temperature of approximately 750°C. Neither longer holding times nor higher temperatures improved magnetization values. Coercive force of films on slide glass (620°C, 30 min) increased with increasing Co content [Fig. 6(a)–(c)], which may be due to their smaller grain size.

A typical example of MMHL is in Fig. 7. We found that the magnetization of our samples was

Table 1. Magnetization M_s of Co doped nickel ferrite thin films at various processing conditions

Temperature and time of annealing (°C) (h)	Type of substrate	Cobalt doping level (%)	Magnetization M_s (mT)
450 1	alumina	1	5–10
500 1	alumina	1	50
650 2	alumina	1	215
750 2	alumina	1	265
900 1	alumina	1	250
625 65	alumina	1	200
625 65	fused silica	1	190
600 0·5	slide glass	2	215
600 0·5	slide glass	4	175
600 0·5	slide glass	10	185

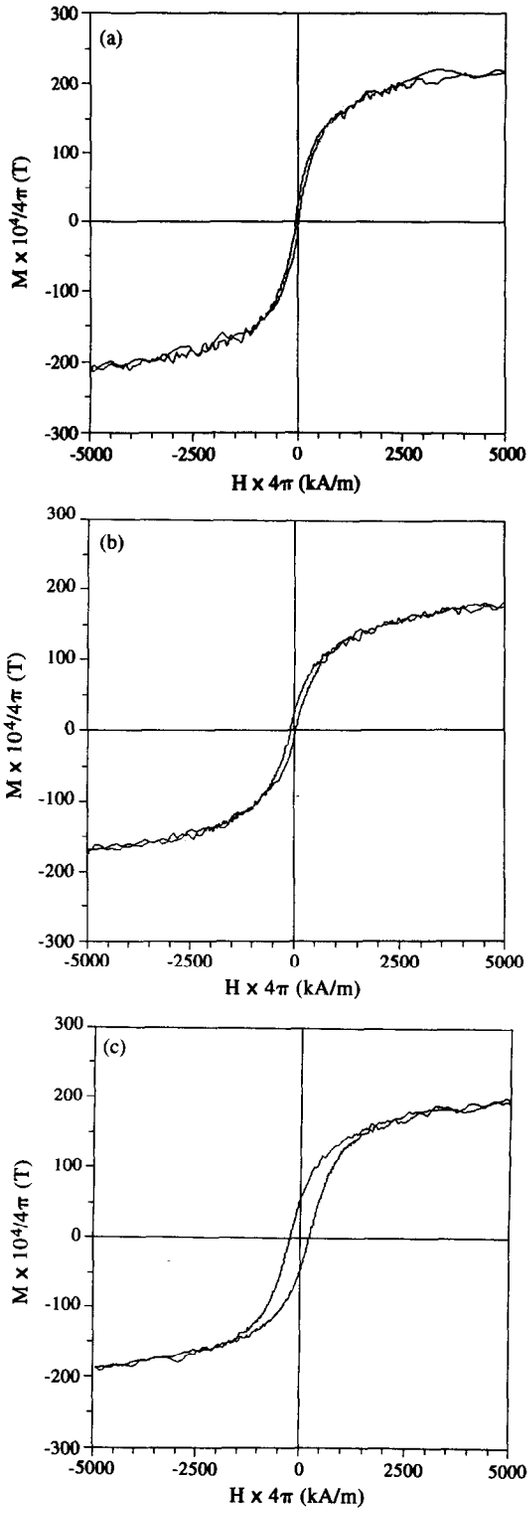

Fig. 6. MHL of $Ni_{1-x}Co_xFe_2O_4$ thin films on glass annealed at 600°C for 3 h in air: (a) x = 0·02, (b) x = 0·04, (c) x = 0·10.

nearly reversible (H_{cm} < 4 A/m) in H_{ext} up to approximately 8 kA/m. For higher applied H_{ext}, hysteresis loops were successively wider and finally overlapped with MHL. Initial susceptibility χ_{MMHL} was smaller than χ_{MHL} by 25%.

3.2.2 MHL data taken on optical fibers

MHL data of the spinel ferrites on optical fibers did not show any substantial difference in a loop

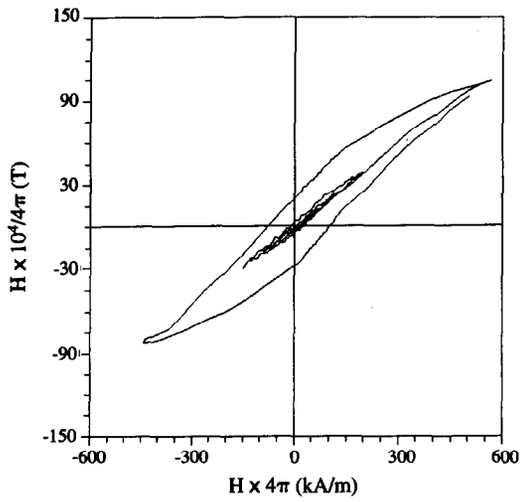

Fig. 7. MHL of $Ni_{0.99}Co_{0.01}Fe_2O_4$ thin film on alumina annealed at 900°C for 3 h in air, low-field sweep.

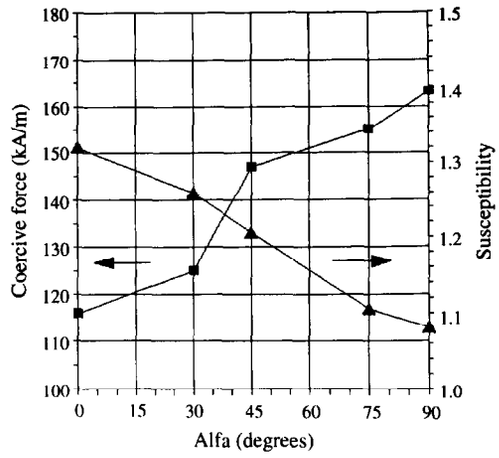

Fig. 9. Coercive force and magnetic susceptibility of $Ni_{0.97}Co_{0.03}Fe_2O_4$ thin film on 125 μm optical fiber as a function of magnetic field direction, arrangement as in Fig. 5(b).

shape with fiber diameter (300, 200 and 125 μm). A rather erratic loop shape was likely due to a different demagnetization factor of the film along the curvature, which was not magnetized uniformly. Interestingly, MHL data of the bundle of fibers revealed fast switching at H close to zero,

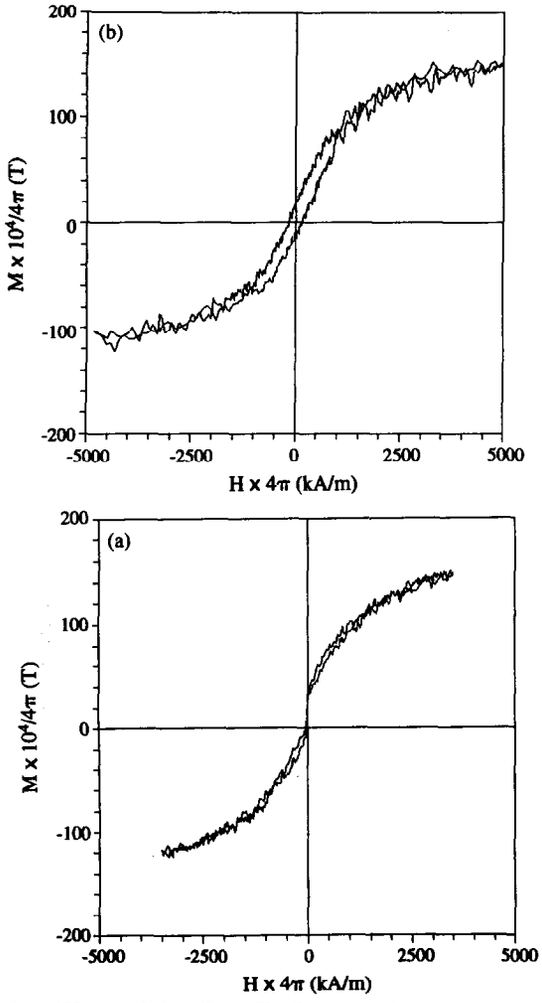

Fig. 8. MHL of $Ni_{0.97}Co_{0.03}Fe_2O_4$ thin film on optical fiber (diameter 125 μm) annealed at 600°C for 2 h in air: (a) arrangement as in Fig. 5(a), (b) perpendicular to the fiber axis, arrangement as in Fig. 5(b).

with a very low coercive force [Fig. 8(a)]. This fact, however, can hardly be utilized from the practical standpoint.

A typical MHL in the second arrangement [Fig. 5(b)] is shown in Fig. 8(b) and its shape changed with the orientation to the magnetic field [angle α in Fig. 5(b)]. From a dependence on coercive force and magnetic susceptibility on a magnetic field direction (Fig. 9), one may conclude that the lowest barrier for domain reorientation exists in directions parallel to a magnetizing field, i.e. in directions along the fiber axis.

MMHL measured on fibers showed that a nearly reversible response on a small (H_{ext} < 2·4 kA/m) magnetic field change can be observed even without preceding AC demagnetization. This fact may be particularly beneficial if a low intensity AC magnetic field is to be detected in an in-line fiber optic magnetometer, thereby neglecting a hysteresis effect. We also conclude that cobalt doped nickel ferrite thin films as a 'hard' magnetic material can be suitable for applications requiring fast magnetic response to low magnetic fields.

4 CONCLUSIONS

(1) Cobalt doped $NiFe_2O_4$ thin films were synthesized using a dip-coating wet-chemical process. The onset of the film crystallization was between 450 and 500°C. Crystallinity increased with increasing processing temperature, and grain size decreased with increasing cobalt content.

(2) Magnetization M_s was a function of the processing temperature and did not improve beyond 700°C. Typical magnetization and coercive forces of $Ni_{0.99}Co_{0.01}Fe_2O_4$ films

(750°C, 2 h) were 265 mT and 15 kA/m, respectively. Magnetization of ferrite films on optical fibers was nearly reversible in external magnetic fields H_{ext} up to about 2·4 kA/m, even without preceding AC demagnetization.

(3) We confirmed that the wet chemical method is also useful for the low temperature synthesis of a ferromagnetic material on optical fibers.

ACKNOWLEDGEMENT

We would like to thank Ing. J. Tlaskal from the Inorganic Institute of the Czech Academy of Sciences for his help in SEM studies. Special thanks are due to Dr V. Matejec for useful discussions throughout this investigation.

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