

# Magnetic softening of Co doped $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> containing residual Fe–Co alloy prepared in low temperature nitridation

Yuji MASUBUCHI,<sup>†</sup> Hiroaki SATO, Teruki MOTOHASHI and Shinichi KIKKAWA

Faculty of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo 060–8628, Japan

Preparation and magnetic properties were investigated on the Co doped  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> obtained in low temperature nitridation of bcc Fe<sub>1-x</sub>Co<sub>x</sub> alloys to change its magnetic coercivity. The alloys were prepared by the reduction of (Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>3</sub>O<sub>4</sub> obtained by hydrolysis of iron and cobalt acetylacetonate mixture in benzyl alcohol. Fine powder of the pure spinel-type (Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>3</sub>O<sub>4</sub> was obtained in  $x = 0–0.05$ . The oxides were reduced to bcc Fe<sub>1-x</sub>Co<sub>x</sub> alloy at 400°C in H<sub>2</sub> gas and then nitrided at 150°C for 5 or 8 h under NH<sub>3</sub> gas flow. XRD and X-ray absorption spectroscopy suggested the nominal “ $\alpha''$ -(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>16</sub>N<sub>2</sub>”, similar to “ $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>” was obtained as a mixture with the residual bcc Fe<sub>1-x</sub>Co<sub>x</sub> alloy at  $x = 0.03$  as in the case of the nitrided product without cobalt. The present nitrided product exhibited a larger magnetization of 217 Am<sup>2</sup> kg<sup>-1</sup> and a smaller magnetic coercivity of 30 mT at  $x = 0.03$  than those for the present products without the Co doping.

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## 1. Introduction

Magnetization of  $\alpha$ -Fe was enhanced by introducing a small amount of nitrogen in low temperature nitridation of  $\alpha$ -Fe fine powder.<sup>1),2)</sup> The nitrided product was a mixture of slightly deformed  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> and a residual  $\alpha$ -Fe.<sup>3)</sup> The maximum magnetization value of 210 Am<sup>2</sup> kg<sup>-1</sup> was observed at the yield of about 60 wt % of the “ $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>”.<sup>2)</sup> Their magnetic coercivity was above 50 mT and increased with the “ $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>” content.<sup>3)</sup> Magnetic coercivity should be decreased or increased to utilize the large magnetization as in either soft or hard magnetic materials.

Cobalt doping into iron compounds has been reported to change their magnetic properties. It is well known that Fe–Co bcc alloy shows a maximum saturation magnetization at around 30 at % of Co content in Slater-Pauling curves.<sup>4),5)</sup> Its magnetic coercivity also changed with Co concentration.<sup>6)</sup> The lowest magnetic coercivity of 1.5 mT was observed at around 8 at % of Co doping, and was about a half of the value for the pure Fe metal. The reduced coercivity was attributed to zero value of the saturated magnetostriction constant for the Fe–Co alloy.<sup>6)</sup> On the other hand, Co doping into  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> increased its coercivity to above 60 mT.<sup>7)</sup> There has been several reports on thin films of cobalt doped iron nitride and theoretical calculations of magnetic property of (Fe,Co) nitride.<sup>8)–11)</sup> To the best of our knowledge, bulk powder product of cobalt doped iron nitride has not yet been reported in a small amount of nitrogen content.

Non-aqueous soft chemical route in benzyl alcohol (BA) solution has been applied to obtain a highly Co doped ZnO.<sup>12),13)</sup> Fine powder mixture of Fe<sub>3</sub>O<sub>4</sub> with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was prepared in similar reaction of iron acetylacetonate [Fe(acac)<sub>3</sub>] with BA with low water solubility having particle size above 40 nm.<sup>14)</sup> The low humidity made the ferromagnetic “ $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>” preparation reproducible in low temperature nitridation of its reduced  $\alpha$ -Fe product.<sup>14)</sup> Co doped Fe<sub>3</sub>O<sub>4</sub> prepared similarly in the hydrolysis

reaction of mixed Fe(acac)<sub>3</sub> and Co(acac)<sub>3</sub> in BA solution might be useful to prepare the Co doped “ $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>” by low temperature nitridation through its reduced Fe–Co alloy.

In the present study, fine powder of (Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>3</sub>O<sub>4</sub> was prepared in BA solution by changing the mixing ratio of Fe(acac)<sub>3</sub> and Co(acac)<sub>3</sub>. Preparation and magnetic properties were investigated to study the magnetic property especially magnetization and magnetic coercivity on the Fe<sub>1-x</sub>Co<sub>x</sub> alloys and their nitrides through low temperature nitridation method starting from the obtained (Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>3</sub>O<sub>4</sub> in relation to their Co content.

## 2. Experimental

(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>3</sub>O<sub>4</sub> were synthesized from Fe(acac)<sub>3</sub> (Extra pure grade, Kanto Chemical Co. Inc.) and Co(acac)<sub>3</sub> (98%, Aldrich) in benzyl alcohol (BA, >99%, Wako Pure Chemical Industries, Ltd.). About 8 g of mixture of Fe(acac)<sub>3</sub> and Co(acac)<sub>3</sub> with Fe:Co molar ratio of (1-x):x ( $x = 0, 0.03, \text{ and } 0.05$ ) was dissolved in 40 mL of BA solution, respectively. The mixed solution was transferred into 100 mL of Teflon container in a steel autoclave. The heat treatment was performed at 200°C for 48 h. The precipitates were washed twice with ethanol and then with acetone. After drying at 60°C, the products were reduced at 400°C for 10 h in H<sub>2</sub> gas flow of 50 mL/min. H<sub>2</sub> gas purity was higher than 99.99% and the reaction tube was 25 mm in diameter as reported in our previous study.<sup>2)</sup> The reduced product was cooled to the room temperature under the H<sub>2</sub> gas flowing. The reaction gas was changed to NH<sub>3</sub> purchased from Sumitomo Seika Chemicals Co. Ltd., with purity of 99.9995% without air exposing the reduced product. The ammonolysis was performed at 150°C for 5 or 8 h under an NH<sub>3</sub> flow of 50 mL/min. The nitrided products were then cooled to room temperature under the NH<sub>3</sub> atmosphere.

The products in the reaction tube were transferred to a glove box with a dew point below –110°C and an oxygen concentration of 0.01 ppm (NM3-P60S, Miwa MGF Co. Ltd.). Magnetization at room temperature was measured on the products sealed in acryl resin capsules, using a vibrating sample magnetometer (BHV-50, Riken Denshi Co. Ltd.) in a magnetic field of

<sup>†</sup> Corresponding author: Y. Masubuchi; E-mail: yuji-mas@eng.hokudai.ac.jp

$\pm 1.5$  T. A superconducting quantum interference device magnetometer (MPMS-5S, Quantum Design) was also used for magnetic measurement in a wider magnetic field of 5 T. Their microstructures were observed by scanning electron microscopy (JSM-6300F, JEOL). The powders were mounted on a carbon tape in the glove box and then transferred into the sample chamber using an air-tight sample carrier. Other part of the nitrided products was slowly exposed to air forming a protective oxide layer on the powder surface to prevent their rapid oxidation. Their crystalline phase was characterized using powder X-ray diffraction (Ultima IV, Rigaku) with monochromated Cu K $\alpha$  radiation. The yield of " $\alpha''$ -(Fe $_{1-x}$ Co $_x$ ) $_{16}$ N $_2$ " was estimated by Rietveld fitting of the PXRD data using the program RIETAN-FP.<sup>15)</sup> The chemical compositions of the oxides, reduced products, and nitrided products were confirmed to be equal to the starting composition  $x$  by fluorescence X-ray spectroscopy (SEA6000VX, SII). X-ray absorption spectra of Fe and Co K-edges were measured in transmission mode at the beam line 9C in Photon Factory, in KEK, Tsukuba Japan. A small amount of sample powder was sandwiched between Scotch tapes. The EXAFS data were analyzed using the program REX-2000 (Rigaku).<sup>16)</sup>

### 3. Results and discussion

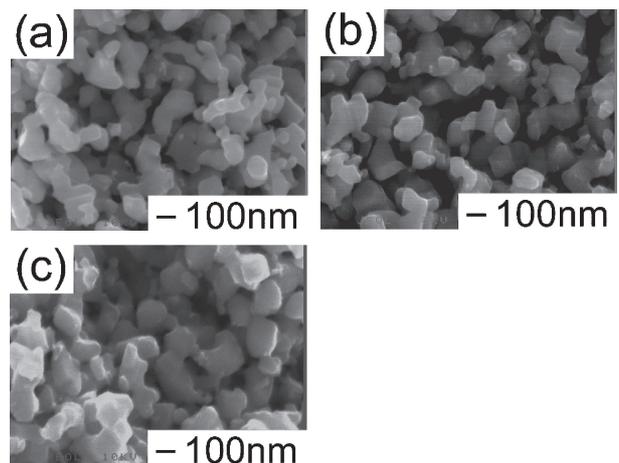
#### 3.1 Preparation of " $\alpha''$ -(Fe,Co) $_{16}$ N $_2$ " by low temperature nitridation

Pure spinel-type (Fe $_{1-x}$ Co $_x$ ) $_3$ O $_4$  ferrite was obtained in the oxides prepared in BA solution similar to our previous study on Fe $_3$ O $_4$  ferrite.<sup>14)</sup> Their crystallite size estimated from the line broadening of the main diffraction peak decreased from 45 nm ( $x = 0$ ) to 30 nm ( $x = 0.05$ ) with increasing Co content. The lattice parameter was  $a = 0.83885(1)$  nm at  $x = 0$ , which was comparable to the reported value of  $a = 0.8394$  nm.<sup>17)</sup> It decreased to  $a = 0.83777(3)$  nm at  $x = 0.05$  along with the Co content. The reported lattice parameter was  $a = 0.8375$  nm for cobalt ferrite, CoFe $_2$ O $_4$ .<sup>18)</sup>

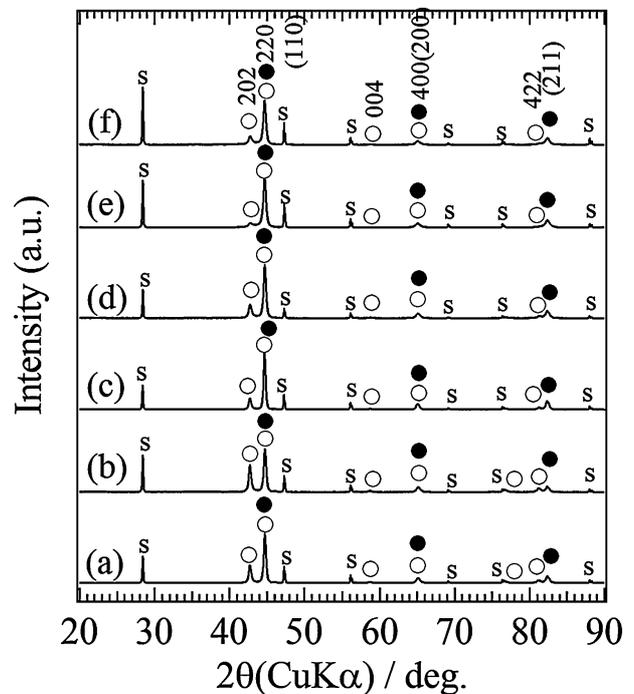
They were reduced to bcc Fe $_{1-x}$ Co $_x$  alloy in phase pure by the firing in H $_2$  flow. Their lattice parameter slightly increased from 0.28665(1) nm at  $x = 0$  to 0.28671(1) nm at  $x = 0.05$  as shown in **Table 1**. SEM observation showed the agglomeration of the bcc alloy powders with similar particle size around 100 nm independently on Co content as shown in **Fig. 1(a)**. The particle size around 100 nm has been suitable for nitridation to  $\alpha''$ -Fe $_{16}$ N $_2$  phase as reported in our previous study.<sup>14)</sup> Saturation magnetization of 195 Am $^2$ kg $^{-1}$  for the reduced  $\alpha$ -Fe ( $x = 0$ ) increased to 206 Am $^2$ kg $^{-1}$  at  $x = 0.05$  similarly to the Slater-Pauling curve as summarized in **Table 1**. The magnetic coercivity decreased on the Co doping and the bcc alloy at  $x = 0.03$  showed the smallest magnetic coercivity of 11 mT. The reported coercivity of Fe $_{1-x}$ Co $_x$  alloy has a minimum value at around  $x = 0.08$  due to the magnetostriction.<sup>5),6)</sup> The larger magnetization and smaller coercivity in the reduced Fe $_{1-x}$ Co $_x$  alloy than  $\alpha$ -Fe may affect on magnetic properties of their nitrided products.

Fine particles of the Fe $_{1-x}$ Co $_x$  alloys were nitrided in low temperature nitridation at 150°C for 5 or 8 h under NH $_3$  flow

without exposing to air. Their morphology was almost unchanged by the nitridation as shown in **Figs. 1(b)** and **1(c)**. The nitrided products were mixture of nominal " $\alpha''$ -(Fe $_{1-x}$ Co $_x$ ) $_{16}$ N $_2$ " and Fe $_{1-x}$ Co $_x$  alloy as shown in **Fig. 2**, similar to our previous nitrided products without Co doping.<sup>2),3),14)</sup> The " $\alpha''$ -(Fe $_{1-x}$ Co $_x$ ) $_{16}$ N $_2$ " yield slightly increased with increasing nitridation duration as summarized in **Table 2**. Maximum yield in 42 wt% of the cobalt doped " $\alpha''$ -(Fe $_{1-x}$ Co $_x$ ) $_{16}$ N $_2$ " appeared at  $x = 0.03$  in 8 h of nitridation duration. However, the yield decreased by increasing Co content. Their lattice parameters were refined to be  $a = 0.5714$  nm and  $c = 0.6288$  nm. Lattice parameters of the " $\alpha''$ -(Fe $_{1-x}$ Co $_x$ ) $_{16}$ N $_2$ " in the mixture did not change significantly



**Fig. 1.** SEM images of the bcc Fe $_{1-x}$ Co $_x$  alloy at  $x = 0.03$  (a), nitrided products at  $x = 0.03$  for 5 h (b) and  $x = 0.05$  for 5 h (c).



**Fig. 2.** XRD patterns for the products nitrided at 150°C (a) for 5 h,  $x = 0$ , (b) for 8 h,  $x = 0$ , (c) for 5 h,  $x = 0.03$ , (d) for 8 h,  $x = 0.03$ , (e) for 5 h,  $x = 0.05$ , and (f) for 8 h,  $x = 0.05$ . Diffraction lines marked with open and filled circles correspond to " $\alpha''$ -(Fe $_{1-x}$ Co $_x$ ) $_{16}$ N $_2$ " and bcc Fe $_{1-x}$ Co $_x$  alloy, respectively. The symbols "s" indicate the diffraction lines of Si reference.

**Table 1.** Saturated magnetization, magnetic coercivity, and lattice parameters for Fe $_{1-x}$ Co $_x$  bcc alloy obtained by reduction of (Fe $_{1-x}$ Co $_x$ ) $_3$ O $_4$

Co composition, $x$	Lattice parameter /nm	Saturated magnetization /Am $^2$ kg $^{-1}$	Coercivity /mT
0.0	0.28665(1)	195	26
0.03	0.28667(1)	206	11
0.05	0.28671(1)	206	14

Table 2. Magnetic properties and phase ratio of the nitrated products

Co composition, $x$	0.0		0.03		0.05	
	5	8	5	8	5	8
Lattice parameters for " $\alpha''$ -(Fe <sub>1-x</sub> Co <sub>x</sub> ) <sub>16</sub> N <sub>2</sub> " phase*						
$a$ /nm	0.57136(2)	0.57137(2)	0.57136(4)	0.57137(4)	0.5714(1)	0.5712(1)
$c$ /nm	0.62888(3)	0.62884(3)	0.62882(5)	0.62882(5)	0.6284(2)	0.6284(1)
" $\alpha''$ -(Fe <sub>1-x</sub> Co <sub>x</sub> ) <sub>16</sub> N <sub>2</sub> " content ( $\alpha''/\alpha''+\alpha$ )/wt %*						
	48.6(2)	63.6(2)	32.8(2)	41.9(4)	23.3(3)	34.4(4)
Saturation magnetization at 5 T/Am <sup>2</sup> kg <sup>-1</sup>	205	210	209	217	206	200
Coercivity/mT	40	44	29	31	29	38

\*These parameters were calculated by Rietveld fitting on the PXRD patterns.

along with the Co content  $x$ . There was no trace of " $\alpha''$ -(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>16</sub>N<sub>2</sub>" in the case of the nitrated Fe<sub>1-x</sub>Co<sub>x</sub> alloy above  $x = 0.10$ . Very small but an obvious diffraction line from Co<sub>2</sub>N was observed in the XRD patterns of products nitrated for 8 h at  $x = 0.10$ . Cobalt and iron are not distinguishable by X-ray diffraction due to similar scattering length. The radii of both elements are quite similar so that the doping does not lead to clear size change of the unit cell. However the nitridation behavior was different in the products from pure Fe<sub>1-x</sub>Co<sub>x</sub> alloys with  $x = 0.0$ , 0.03 and 0.05. Their magnetic study clarify the behavior of cobalt in the nitridation.

X-ray absorption spectra of Fe and Co K-edges were taken on the nitrated products to investigate the local structural change around both Fe and especially Co atoms. The radial distributions were calculated by the Fourier transform of the EXAFS region. Bonding around Fe/Co atoms appeared at around 0.21 nm for the nitrated product at  $x = 0$  and 0.03, although the nearest interatomic distances were about 0.22 nm for Fe/Co respective metal before nitridation as shown in Figs. 3(a) and 3(e). Bond lengths between Fe atoms have been reported to be 0.248 nm in  $\alpha$ -Fe and 0.244 nm in  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>.<sup>3),19)</sup> The observed bond shrinkage corresponds to the formation of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> phase in the nitrated product. Longer nitridation duration of 8 h did not change significantly the distribution around Fe/Co atom at  $x = 0.03$ . However the corresponding bond distance around Co increased to 0.225 nm for the 5% Co doped product, although there was not much change around Fe atoms as shown in Figs. 3(d) and 3(g). The peak shift and different distribution around Co at  $x = 0.05$  imply the appearance of partial phase decomposition from bcc " $\alpha''$ -(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>16</sub>N<sub>2</sub>" to hcp Co<sub>2</sub>N. Cobalt atoms are incompatible in  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> lattice with body-centered iron stacking, when their concentration is enough to form a Co nitride like cluster in the nitrated product. Local structure around the Co atom in the nitrated products at  $x = 0.05$  might be distorted to decompose into hcp lattice, although such local structural distortion did not change the XRD pattern significantly because the abundant iron atoms in the nitrated products had body-centered lattice. Distances between Co atoms are 0.250 nm in hcp Co metal and 0.263 nm in Co<sub>2</sub>N.<sup>20),21)</sup> They are longer than Fe-Fe distance of 0.244 nm in  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>.<sup>3)</sup>

### 3.2 Magnetic property of " $\alpha''$ -(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>16</sub>N<sub>2</sub>"

The magnetic hysteresis of the nitrated products was not saturated under 1.5 T of magnetic field as shown in the inset of Fig. 4. It was saturated in a larger magnetic field above 3.0 T as reported in our previous study.<sup>3)</sup> The nitrated products in Table 2 showed a slightly larger magnetization values than those for the alloys before nitridation in Table 1. Magnetic coercivity was smaller in the product at  $x = 0.03$  than those of the products without Co doping. Magnetic property changed depending on the

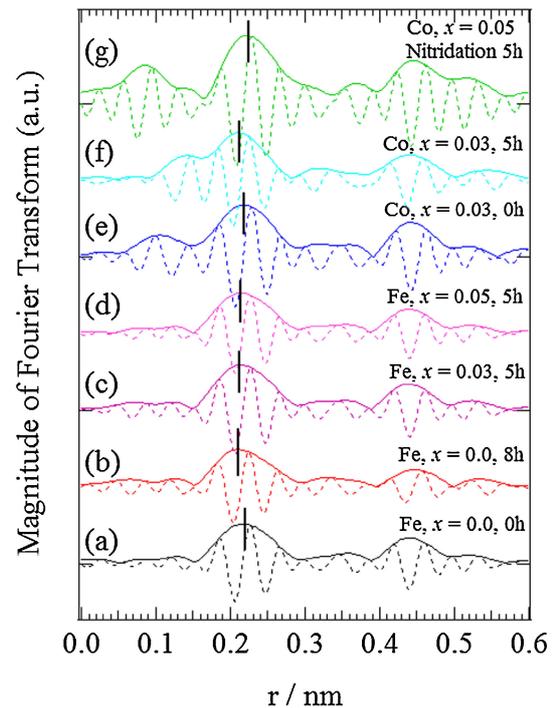


Fig. 3. Fourier transforms of the Fe K-edge EXAFS spectra of the alloy (a) at  $x = 0.0$  and the nitrated products (b) at  $x = 0.0$ , nitridation duration of 8 h, (c) at  $x = 0.03$ , 5 h, (d) at  $x = 0.05$ , 5 h, and Co K-edge spectra for the alloy (e) at  $x = 0.03$  and the nitrated products (f) at  $x = 0.03$ , 5 h and (g) at  $x = 0.05$ , 5 h. Thick lines were drawn as indicators for the distances from Fe/Co atom to metallic atoms (Fe and Co) in the products.

Co content in the nitrated mixtures of " $\alpha''$ -(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>16</sub>N<sub>2</sub>" and the residual bcc Fe<sub>1-x</sub>Co<sub>x</sub> alloys as reported on Fe-Co alloys with a small Co content. However magnetization decreased and the coercivity increased on the nitrated products at  $x = 0.05$ . Paramagnetic Co<sub>2</sub>N observed on the product with  $x = 0.10$  might begin to precipitate even in the less Co product at  $x = 0.05$ .

The magnetization of the nitrated products may change with an increase in magnetic moment on Fe sites occupied by Co as in the case of Slater-Pauling curve. The Co substitution for Fe site also changes the average magnetostriction value,  $\lambda_{AVE}$ , close to zero at  $x = 0.03$  as shown in Fig. 5. The  $\lambda_{AVE}$  is estimated from the saturated magnetostriction constants  $\lambda_{100}$  and  $\lambda_{111}$  reported on a Fe-Co single crystal directed to [100] and [111] in cubic lattice, respectively, by using the following equation.<sup>22),23)</sup>

$$\lambda_{AVE} = 2/5\lambda_{100} + 3/5\lambda_{111}$$

It can be related to the magnetoelastic energy,

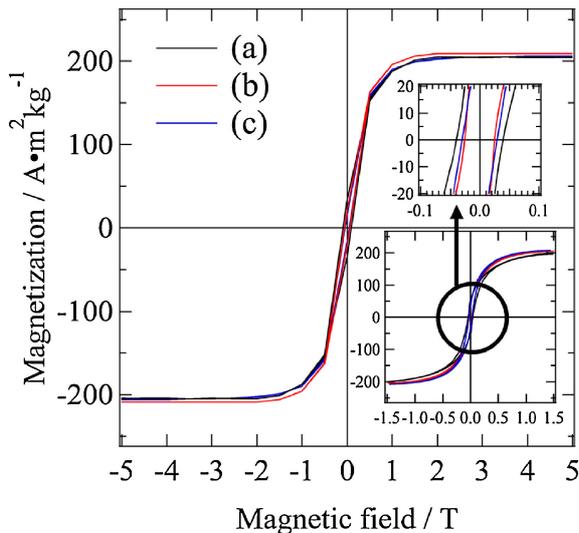


Fig. 4. Magnetic hysteresis of the nitrided products at (a)  $x = 0$ , (b)  $x = 0.03$  and (c)  $x = 0.05$  obtained in nitridation duration of 5 h. Inset shows curves in a  $\pm 1.5$  T field.

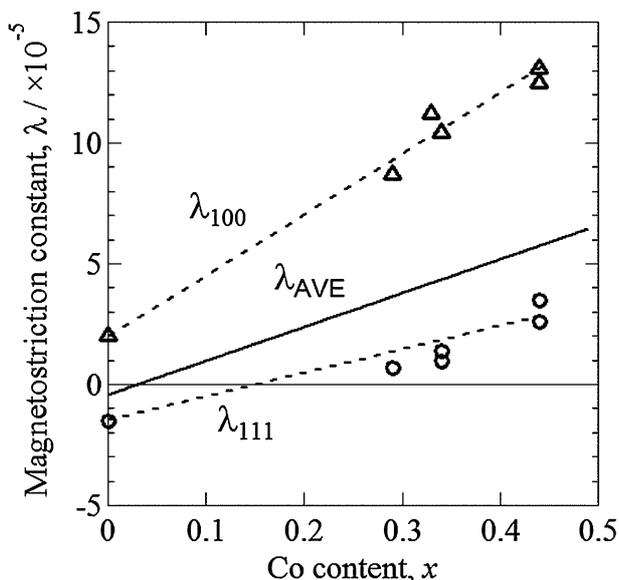


Fig. 5. Magnetostriction constants for  $\text{Fe}_{1-x}\text{Co}_x$  alloy. The data points for  $\lambda_{100}$  and  $\lambda_{111}$  were plotted by using magnetostriction constants of Fe-Co single crystals.<sup>22)</sup> The averaged magnetostriction,  $\lambda_{\text{AVE}}$  was calculated as describing in the main text.

$$E_{me} = 3/2 \lambda_{\text{AVE}} \cdot \sigma \cdot \sin^2 \theta$$

where  $\theta$  is the angle between magnetization and  $\sigma$  is the applied stress.<sup>23)</sup> Reduction of magnetostriction,  $\lambda_{\text{AVE}}$ , minimizes a magnetoelastic energy to decrease the magnetic coercivity. The  $\lambda_{\text{AVE}}$  value of the  $\text{Fe}_{1-x}\text{Co}_x$  alloy linearly changes from negative to positive against Co content as shown in Fig. 5. The value of  $\lambda_{\text{AVE}}$  is zero at  $x = 0.03$  in the  $\text{Fe}_{1-x}\text{Co}_x$  alloy. The minimum coercivity was observed in the present nitrided products at  $x = 0.03$  as in the case of the alloy. The zero value observed in the alloy may similarly contribute to reduce the magnetic coercivity in the nitrided product with the Co substitution, although further substitution lead to the formation of  $\text{Co}_2\text{N}$ . The present way to change the magnetic coercivity will be useful to realize the

application of  $\alpha''\text{-Fe}_{16}\text{N}_2$  as a practical magnetic material.

#### 4. Conclusions

Co doped  $\alpha''\text{-Fe}_{16}\text{N}_2$  was prepared by low temperature nitridation of  $\text{Fe}_{1-x}\text{Co}_x$  alloy reduced from  $(\text{Fe}_{1-x}\text{Co}_x)_3\text{O}_4$  obtained in benzyl alcohol. The yield of " $\alpha''\text{-}(\text{Fe}_{1-x}\text{Co}_x)_{16}\text{N}_2$ " in the nitrided mixtures with residual  $\text{Fe}_{1-x}\text{Co}_x$  alloy increased with the nitridation duration but decreased with an increasing Co content. Magnetic coercivity was successfully reduced to 30 mT in the nitrided products at  $x = 0.03$  keeping a large magnetization of  $217 \text{ Am}^2 \text{ kg}^{-1}$ .

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