Whisker-Like Goethite Nanoparticles Containing Cobalt Synthesized in a Wet Process

Kazuharu Iwasaki and Tsutomu Yamamura

1 Sendai Technology Center, Sony Corporation, Tagajo 985-0842, Japan
2 Department of Metallurgy, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Acicular α-FeOOH particles are formed through aging of ferric oxyhydroxide colloidal solution formed by the neutralization of FeCl₃ aqueous solution by NaOH. The effects of cobalt ion addition in the sol–gel–sol process on the formation rate and morphology of α-FeOOH nanoparticles have been investigated. The magnetic properties of metal nanoparticles prepared from the obtained particles have also been examined. The dependence of reaction rate constants in the formation of α-FeOOH in the wet process and the crystallite size of (110) on Co content in α-FeOOH has been made clear. Both the rate constant and crystallite size decrease with increasing Co content in α-FeOOH particles. The negative zeta-potential of the formed α-FeOOH particles increases slowly with increasing pH of the electrolytic solution. The negative zeta-potential of α-FeOOH particles containing Co is larger than that of α-FeOOH particles without Co in the range of pH 6–pH 12. The relationship between the morphology of the formed α-FeOOH particles and the cobalt content in α-FeOOH particles has been investigated. The length of major axis increases and the length of minor axis decreases with increasing Co content, and the aspect ratio increases remarkably. It is likely that Fe(OH)₃ complex ion precipitates preferentially on the c plane, and the particles grow remarkably in the direction of c axis. The interplanar spacing of the α-FeOOH decreases with increasing Co content. The formed α-FeOOH grows abnormally like whisker in the direction of major axis: c axis in the case of significantly much Co content: 27 at%, and also the whisker like nanoparticles are observed to grow with curving. The magnetic metal nanoparticles produced have excellent dispersivity and high aspect ratio. The metal nanoparticles have magnetic properties enough for the magnetic recording media.

Keywords: goethite nanoparticle, cobalt content, zeta-potential, rate constant, crystallite size, cobalt ion, selective adsorption, particle morphology, magnetic metal nanoparticle

1. Introduction

In the production process of magnetic recording media, acicular α-FeOOH particles are utilized as raw materials. In the industrial processes, those particles are dehydrated by heating, and reduced to obtain fine magnetic metal particles. To attain high performance of the magnetic recording media, monodispersed, fine and acicular shaped metal particles are required as raw materials. It is well known that the properties of fine metal particles for the magnetic recording media are controlled by the extent to which the metal particles keep the acicular shape of the original α-FeOOH particles. For that, it is important to establish a shape control method of performing monodispersion and fine particle size refinement while keeping the acicular shape of the α-FeOOH particles.

Acicular α-FeOOH particles are formed through aging of amorphous ferric oxyhydroxide colloidal mother solution formed by the neutralization of FeCl₃ aqueous solution by NaOH (sol–gel–sol process).1-6 The addition of foreign ions to the mother liquid can be considered as one of the available shape control methods for α-FeOOH particles. As for anions, the adsorption mechanism of phosphate, sulfate and carbonate ions on the α-FeOOH crystalline surface has been reported.7-11 Moreover, as for cations, the effects of the doping of metal ions such as Cu²⁺, Zn²⁺, Mn²⁺, Ni²⁺ and Cr³⁺ into α-FeOOH crystal lattice have been reported.12-15 However, those studies did not aim the shape control of α-FeOOH particles.

In the present study, the effects of cobalt ion addition in the sol–gel–sol process on the formation rate and morphology of α-FeOOH nanoparticles have been investigated. Furthermore, the magnetic properties of metal nanoparticles prepared have also been examined.

2. Experimental Procedure

2.1 Sample preparation

The special grade reagent FeCl₃ · 6H₂O and reagent CoCl₂ · 6H₂O were used for the preparation of the ferric and cobalt ionic solutions, respectively. The 0.375 kmol m⁻³ and 0.075 kmol m⁻³ NaOH solutions were also prepared from a special grade reagent NaOH. The FeCl₃ solution of 2.5 × 10⁻³ m⁸, CoCl₂ solution and the two kinds of NaOH solutions in a predetermined quantity were mixed through a batch operation to obtain the mixed suspensions. The mixed suspensions were stirred in a homogenizer for 5 min and neutralized, and a brown-red suspension was obtained at 23–24°C. The pH of the suspension was adjusted to 11.2–13.0. The FeCl₃ concentration of the suspensions was kept constant within the range of 0.038–0.041 kmol m⁻³. The CoCl₂ concentration of the suspensions was conditioned so as the mole ratio of Co/Fe to be within the range of 0.02–0.25.

After the suspensions were aged in a thermal chamber at 45–80°C for 2–337 h, slurry was obtained. The slurry was washed with a high purity ion-exchange water up to the level at which the pH and electrical conductivity of the filtrate became equal to or less than 8.0 and equal to or less than 10.0 × 10⁻³ µS m⁻¹, respectively. After the raffinate was dehydrated at 80°C for 12–24 h in a dryer and was ground to powder by a mortar, they were used as sample for the further.
TG/DTA6300 and EXATAR6000 thermal analysis system (Seiko Instruments Inc.) was used for the TG and DTA analyses. The formed particles were then dehydrated by heating at 823 K for 10 min in N₂ and reduced at 813–893 K for a predetermined time in 50 mol%H₂–50 mol%Ar. The obtained metal nanoparticles were slowly oxidized partially at 315 K for the given time in 0.5 mol%O₂–99.5 mol%N₂ to prevent the samples from ignition in atmosphere. The magnetic paints were prepared by mixing and dispersing the magnetic metal powders, the mixtures of urethane and vinyl chloride and the organic solvents in a predetermined quantity. The magnetic films were also produced by orientating particles in the direction of coating in the d-c magnetic field: 500 mT.

2.2 Measurements of powder properties

The formed particles were examined by an X-ray powder diffraction method (XRD) and a TEM observation. The X-ray diffractometer RAD-II X (Rigaku Denki inc.) was used, and the measurements were carried out under the conditions of 40 kV and 40 mA using the X-ray tube of CoKα1. The crystallite size of the particles was calculated from the Scherrer’s equation based on the diffraction patterns from 22.0° to 26.0°. Silicon powder with the mean particle size of 10 μm and a purity of 99.9 mass% was used as an external reference and also the diffraction patterns were measured over a scanning range of 30.0°–38.0°. TEM observation was done by a JEM-200CX (JEOL). Distributions of major axis, minor axis and aspect ratio of the formed particles were calculated from the observed TEM photographs. The particle distributions were statistically analyzed on 300 particles.

In this study, XRD was used for measuring the concentration of α-FeOOH particles produced from the amorphous ferric oxyhydroxide gel in the suspension. The silicon powder with the mean particle size of 10 μm and a purity of 99.9 mass% was used as an external reference material to calculate the concentration of α-FeOOH particles. Equivalent amounts of the silicon powder were uniformly mixed with the formed particles. An integral strength ratio according to the maximum peak intensity for the 110 reflection in the α-FeOOH particles and the diffraction peak in silicon powder was calculated. The concentration of α-FeOOH particles was calculated from the calibration curve indicating the relationship between the integral strength ratio and the concentration. The diffraction patterns of the formed particles and silicon powder were measured over the scanning range of 22.0°–27.0° and 32.0°–34.0°, respectively. The cobalt contents in α-FeOOH particles were quantitatively measured by the X-ray fluorescence analysis. The well milled α-FeOOH powders were pressed and molded into the disk: 42 mm in diameter and 5 mm thick under the condition of 1.47 × 10⁵ N and for 20 s. Diameter of the analyzing X-ray was 30 mm. The calibration curve indicating the relationship between the integral strength ratios of Co/Fe and the Co contents in α-FeOOH was previously prepared by the use of the samples with known Co contents. The standard samples used for the calibration were prepared as follows. Both α-Fe₂O₃ powders and CoO powders of 99.9 mass% were well milled and mixed. The standard samples were prepared by pressing and molding those mixed powder of 5, 10, 15, 20, and 30 at% Co. After the X-ray fluorescence analysis, the standard samples were dissolved into HCl solution. The solutions were diluted to give 1 ppm solution, and analyzed by an inductively coupled plasma atomic emission spectroscopy (ICP-AES). A SPS1200VR (Seiko Densi Inc.) was used for ICP-AES. A 3370E (Rigaku Denki Inc.) was used for the fluorescent X-ray analysis. A LiF for the spectral crystal, the Fe–Kα and Co–Kα for the analytical lines were used. The zeta-potential on α-FeOOH surfaces was measured by LASER ZEEth Model 501 (PenKem inc.).

The magnetic properties of the metal nanoparticles and the coated films were also measured by VSM (Toei Kogyo Inc.) for the stamped sample with apparent density of 10³ kg·m⁻³ and with the external magnetic fields of 1.2 MA·m⁻¹ for the metal nanoparticles and 400 kA·m⁻¹ for the coated films.

3. Results and Discussions

3.1 Effects of addition of cobalt ion on formation rate and crystallite size

The effect of quantity of cobalt ion added to the colloidal mother liquid on the formation of α-FeOOH particles has been investigated. The relationship between the concentration of α-FeOOH crystalline particles and the aging time is shown in Fig. 1. A FeCl₃ concentration and pH of the mother liquids are 0.039 kmol·m⁻³ and 12.0, respectively, and aging temperature is 45°C. The range of Co content is 0–14.2 at% with respect to Fe. Through aging the concentration of α-FeOOH crystalline particles increased firstly, and then approached a constant value. The increasing rate of the concentration of α-FeOOH crystalline particles obviously decreased with increasing Co contents.

The formation reaction of the crystalline α-FeOOH particle grown from the amorphous ferric oxyhydroxide gel can be expressed as follows: 

\[
\begin{align*}
\text{FeO}_x(\text{OH})_{3-2x}(\text{amor.}) + x\text{H}_2\text{O} + \text{OH}^- & \rightarrow \text{Fe}(\text{OH})_4^+ \\
\text{Fe}(\text{OH})_4^- & \rightarrow \alpha-\text{FeOOH(crys.)} + \text{H}_2\text{O} + \text{OH}^- 
\end{align*}
\]

Equations (1) and (2) yield eq. (3) for the crystalline α-FeOOH formation.

\[
\text{FeO}_x(\text{OH})_{3-2x}(\text{amor.}) \rightarrow \alpha-\text{FeOOH(crys.)} + (1 - x)\text{H}_2\text{O}
\]

Fig. 1 Relationship between mole fraction of crystalline α-FeOOH particles x and aging time t. FeCl₃ concentration, pH and aging temperature of mother liquids are 0.039 kmol·m⁻³, 12.0 and 45°C, respectively.
When the unstable amorphous ferric oxyhydroxide is dissolved into the colloidal solution, the complex ion $\text{Fe(OH)}_2^-$ is formed. Then, the $\alpha$-FeOOH crystalline particles are reprecipitated when the concentration of the complex ions are supersaturated.

The rate equation of primary reaction as shown in eq. (4) can be applicable to the formation reaction of $\alpha$-FeOOH crystalline particles.$^{1-6,19}$

$$\ln(1 - x) = -kt \quad (4)$$

The results shown in Fig. 1 were analyzed by the reaction rate eq. (4), and the relationship between $-\ln(1 - x)$ and $t$ is shown in Fig. 2. The rate equation of primary reaction reproduces the good linearity observed. The reaction rate constant $k$ was calculated from the slope of the straight line. The rate constant is plotted against Co content in Fig. 3. The rate constant monotonically decreases with increasing Co contents.

The crystallite size of $\alpha$-FeOOH particles was calculated from the full width at half maximum (FWHM) of the (110) reflection of the $\alpha$-FeOOH particles by applying Scherrer’s equation shown in eq. (5),

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos \theta} \quad (5)$$

where $D_{hkl}$, $\beta$, $\theta$ and $\lambda$ are the mean crystallite size, the FWHM, the Bragg angle and the wave length of characteristic X-rays, respectively. The crystallite size in the ⟨110⟩ direction, $D_{110}$ agrees with the length of minor axis of the acicular $\alpha$-FeOOH particles determined by TEM. The dependence of crystallite size on Co contents is shown in Fig. 4. The crystallite size decreases with increasing Co content, and is independent of pH and aging temperature.

A zeta-potential on the surfaces of the formed $\alpha$-FeOOH particles measured by the electrophoresis method is plotted against pH in Fig. 5. Concentration of NaCl was kept constant at $1 \times 10^{-3}$ kmol·m$^{-3}$. In the figure, the case without Co is shown for comparison. In either case, the zeta-potential changes from positive values to negative values, and the negative potential increases slowly with increasing pH of the electrolytic solution. The negative potential of $\alpha$-FeOOH particles containing Co is larger than that without Co in the range of pH6–pH12. The isoelectric points of the particles containing Co and those without Co are pH7.5 and pH10.5.

The dependences of rate constant and crystallite size on the Co content shown in Figs. 3 and 4, respectively, may be considered in the following way. The surface of $\alpha$-FeOOH containing Co has the larger negative potential in the range of high alkalinity as shown in Fig. 5. The $\alpha$-FeOOH surface is coated with $\text{OH}^-$ ion, and has the negative charges in the range of alkalinity. The Co ions doped into the crystalline $\alpha$-FeOOH are substituted into Fe site and causes the negative increase in zeta potentials with an increase in pH as shown.
in Fig. 5. The surface has the great negative charges, and the negative zeta potential increases. The OH\(^-\) ion especially is exclusively adsorptive to the side-planes: a and b planes parallel to the c axis which occupies most of the whole surfaces of \(\alpha\)-FeOOH particles. The rate constant \(k\) of the formation of \(\alpha\)-FeOOH decreases with an increase in Co content because the crystal growth of the a and b planes is blocked according to the peculiar-adsorption of OH\(^-\) ion. The crystallite size of (110) indicating the direction of side-plane parallel to the c axis decreases. Also in the platelet-type hematite particles, the similar behavior on the peculiar-adsorption of OH\(^-\) ion was reported by Sugimoto et al.\(^{20,21}\)

According to Inouye et al.,\(^{12}\) the crystal growth of \(\alpha\)-FeOOH is blocked and the crystallite size of (110) decreases with increasing Cu addition quantity. The formed particles were not crystallized and the \(\alpha\)-FeOOH crystal structure was not formed above 2.5 at% (Cu/Fe).\(^{12}\) In the case of \(\gamma\)-FeOOH, the crystal growth was blocked and the crystallite size of (020) decreased.\(^{13}\) Also in the case of Zn addition, \(\alpha\)-FeOOH crystal structure was distorted by increasing the addition quantity, and a spinel structure was formed above 23.0 at% (Zn/Fe) as reported by Inouye et al.\(^4\) The crystallite size of (110) of \(\alpha\)-FeOOH decreases by the Zn addition. The same tendency was also observed in the case of Mn addition. In the case of Ni addition, the products other than \(\alpha\)-FeOOH were also observed above 14.5 at% (Ni/Fe). The spinel structure was not observed, but \(\alpha\)-FeOOH was observed up to 46.7 at%. The crystallite size decreased firstly, and increased with increasing the addition quantity of Ni. The ability which inhibited the crystal growth of \(\alpha\)-FeOOH and destroyed the \(\alpha\)-FeOOH crystal structure increased in the following order: Cu(II) > Zn(II) > Mn(II). According to a Raman spectrum of the \(\alpha\)-FeOOH containing Cr formed by a Cr addition, the \(\alpha\)-FeOOH structure was destroyed and refined with increasing the Cr addition quantity.\(^{15}\) A Co content dependence of the structural change of \(\alpha\)-FeOOH in the present study is similar to the behavior observed for the cases of Zn and Mn additions.

### 3.2 Effect of addition of cobalt ion on the morphology of formed Goethite nanoparticles

The changes of morphology and structure in the formed \(\alpha\)-FeOOH particles with the addition of Co ion to mother liquid have been investigated. The relationship between the morphology of the formed particles observed by TEM and the Co contents of \(\alpha\)-FeOOH is shown in Fig. 6. The shape of the formed \(\alpha\)-FeOOH particles gradually changes from the plate to the slender needle grown in the direction of the major axis and blocked in the direction of the minor axis with increasing the Co content.

The morphology change of the formed \(\alpha\)-FeOOH particles was observed by TEM, and a distribution of the particle size was quantitatively calculated based on the TEM photographs. The cumulative distributions of the length of major and minor axes and the aspect ratio of the formed particles were analyzed. The relationship between them and Co content of the particles is shown in Fig. 7. The length of major axis increases and the length of minor axis decreases with increasing Co content. In consequence, the aspect ratio increases remarkably with the change in Co content. In the case of 14.2 at% Co content, the cumulative mean value of the aspect ratio increases from 4 to 24.

The interplanar spacing of the formed \(\alpha\)-FeOOH was measured by XRD. The dependence of interplanar spacing on cobalt content in \(\alpha\)-FeOOH particles is shown in Fig. 8. The interplanar spacing \(d\) is normalized by the spacing without Co addition in the figure. The interplanar spacing decreases with increasing Co content in either crystal plane. The decrease of interplanar spacing of the c plane: (002) is the largest, but that of the b plane: (020) is the smallest. The anisotropy in the lattice distortions of each crystal plane was observed. Such behavior means that the \(\alpha\)-FeOOH crystal lattice is strained by the compressive forces with increasing the Co content. Namely, in the process which Co\(^{2+}\) ions in the lattice distortions of each crystal plane were picked up into the \(\alpha\)-FeOOH crystal lattice, it may be considered that Co\(^{2+}\) ions are oxidized to form Co\(^{3+}\) ions, and then, substitute with Fe\(^{3+}\) ions in the lattice. As the ionic radius of Co\(^{3+}\): 63 pm, is smaller than that of Fe\(^{3+}\): 64 pm, the crystal lattice may undergo the compressive forces. However, as the ionic radius of Co\(^{2+}\) is 72 pm larger than Fe\(^{2+}\) radius, the direct substitution of Co\(^{2+}\) ions with Fe\(^{3+}\) ions would not explain the results shown in Fig. 8. Such behavior of lattice distortion by the cobalt ion addition has not been found in the literatures.

Such morphology change of the formed particles shown in Figs. 6 and 7 is considered to be caused by the selective ad-
Whisker-Like Goethite Nanoparticles Containing Cobalt Formed in a Wet Process

Fig. 7 Lengths of major axis (a), minor axis (b) and aspect ratio (c) of acicular α-FeOOH particles at various cobalt content. FeCl₃ concentration, pH and aging temperature of mother liquid are 0.039–0.041 kmol·m⁻³, 12.5 and 60°C, respectively.

Absorption of OH⁻ ion on the a and b planes parallel to the c axis of α-FeOOH particles. The crystal growth of a and b planes is blocked because the precipitation of solute: Fe(OH)₄⁻ complex ion is hindered. In consequence, Fe(OH)₄⁻ complex ion precipitates preferentially on the c plane of α-FeOOH. Another controlling factor can also be considered for the morphology change of those particles. As previously shown in Fig. 8, the substitution of Fe³⁺ ions with Co³⁺ ions in the lattice reduces the interplanar spacings of a, b and c planes, but most significant in c plane. When Fe(OH)₄⁻ complex ion is integrated into the α-FeOOH crystalline phase, the distorted c plane might bring in the misfit with the Fe(OH)₄⁻ complex ion on a and b planes, and consequently inhibit the growth of a and b planes. Therefore the particles grow remarkably in the direction of c axis, and the formed α-FeOOH was shaped into slender acicular particles with the great aspect ratio when Co was added.

Fig. 8 Dependence of normalized interplanar spacing d on cobalt content in α-FeOOH particles. FeCl₃ concentration, pH and aging temperature of mother liquid are 0.039–0.041 kmol·m⁻³, 12.0 and 45°C, respectively.

Fig. 9 X-ray diffraction patterns of formed particles (CoKα). Cobalt content is 16.4 at%. FeCl₃ concentration, pH and aging temperature of mother liquid are 0.038 kmol·m⁻³, 12.5 and 80°C, respectively.

Besides acicular α-FeOOH particles, cubical particles were observed by TEM in the case of Co content above 16 at%. According to XRD pattern shown in Fig. 9, Fe₂O₃ was detected besides α-FeOOH of orthorhombic system. The observed cubic particles may be Fe₂O₃ of spinel structure and/or Co ferrite substituted partially with Co²⁺ ion. The formation of particles of spinel structure was confirmed in the case of Co addition in the present study. This agrees with the results reported by Ishikawa et al. for Zn and Mn additions. It may be considered that Co ferrites of spinel structure were formed when the Co²⁺ ion content exceeded the solubility of Co³⁺ ions in α-FeOOH.

The morphology of the particles prepared under large Co content is shown in Fig. 10. The Co content in α-FeOOH is 27 at%. The formed α-FeOOH grew abnormally in the direction of major c axis like whisker. Moreover, the whisker like nanoparticles grew with curving to the size of several µm in c axis. The reason of curvature growth of whisker like nanoparticles is not obvious at present. Nevertheless, it may be considered that in the case of α-FeOOH doped with Co³⁺ ions in large quantities, the interplanar spacings of the a and b planes decrease remarkably, and then the crystal lattice undergoes great strain. Consequently, the growth direction of α-FeOOH may be considered to be curved by the accumulated misfit caused by strain on the crystal plane.
Fig. 10 Morphology of whisker-like $\alpha$-FeOOH particles containing Co. Cobalt content is 27 at%. FeCl$_3$ concentration, pH and aging temperature of mother liquid are 0.037 kmol·m$^{-3}$, 12.5 and 80°C, respectively.

Fig. 11 Comparison of shapes between raw $\alpha$-FeOOH particles (a), (b), (c) and metal particles (d), (e), (f). Cobalt contents in raw $\alpha$-FeOOH particles are (a) without addition, (b) 2.2 at% and (c) 6.5 at%.

3.3 Preparation of magnetic metal nanoparticles made from acicular Goethite nanoparticles

The acicular magnetic metal nanoparticles were prepared from the $\alpha$-FeOOH particles prepared in the present study through the dehydration by heating and reduction by hydrogen. The dehydration was carried out at 823 K in N$_2$. The reduction was carried out at 813–893 K in 50%H$_2$–50 mol%Ar mixture. The reduced metal particles were oxidized partially at 315 K in 0.5 mol%O$_2$–99.5 mol%N$_2$ mixture to stabilize the surface. The shapes of the acicular magnetic metal nanoparticles observed by TEM are compared with those of the raw $\alpha$-FeOOH particles in Fig. 11. Each metal nanoparticle maintains the shape of the $\alpha$-FeOOH precursor. The length of major axis of $\alpha$-FeOOH particles increases with increasing the Co content, and correspondingly the length of major axis of the formed metal nanoparticles also increases. The cumulative distributions of the lengths of major and minor axes and aspect ratio of the acicular metal nanoparticles are shown in Fig. 12. The length in major axis increases with increasing Co content, on the other hand the length in minor axes little change. Consequently, the aspect ratio increases with increasing Co content. The median diameters of major and minor axes are 130–290 nm and 22 nm, respectively, and the median aspect ratios are 6–13 for the metal nanoparticles.

The magnetic properties of acicular metal nanoparticles were measured for the metal powders prepared and listed in
Table 1. Magnetic properties of acicular metal nanoparticles produced from raw \( \alpha \)-FeOOH nanoparticles.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation magnetization ( \sigma/\mu\text{Wb-m-kg}^{-1} )</td>
<td>151</td>
<td>152</td>
<td>166</td>
</tr>
<tr>
<td>Squareness ratio ( \sigma/\alpha ) (—)</td>
<td>0.492</td>
<td>0.500</td>
<td>0.502</td>
</tr>
<tr>
<td>Coercivity ( H_c/\text{kA-m}^{-1} )</td>
<td>118.8</td>
<td>129.3</td>
<td>131.9</td>
</tr>
<tr>
<td>Packing density ( \rho/10^3 \text{kg-m}^{-3} )</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Particle size</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major axis, ( l/\mu\text{m} )</td>
<td>130</td>
<td>190</td>
<td>290</td>
</tr>
<tr>
<td>Minor axis, ( l/\mu\text{m} )</td>
<td>21</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Aspect ratio (—)</td>
<td>6.0</td>
<td>8.5</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Table 2. Magnetic properties of coated films of acicular metal nanoparticles.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation magnetic flux density ( B_r/\text{mT} )</td>
<td>266.1</td>
<td>252.0</td>
</tr>
<tr>
<td>Residual magnetic flux density ( B_r/\text{mT} )</td>
<td>238.3</td>
<td>228.9</td>
</tr>
<tr>
<td>Squareness ratio ( B_r/B_s ) (—)</td>
<td>0.895</td>
<td>0.908</td>
</tr>
<tr>
<td>Coercivity ( H_c/\text{kA-m}^{-1} )</td>
<td>119.9</td>
<td>134.0</td>
</tr>
<tr>
<td>Switching field distribution (—)</td>
<td>0.672</td>
<td>0.656</td>
</tr>
<tr>
<td>Coating thickness ( t/\mu\text{m} )</td>
<td>3.6</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 1. The magnetic paints were prepared from the metal powders, and coated on PET films. The magnetic properties of coated films were measured, and listed in Table 2. The squareness ratios are as high as 0.89–0.91, in spite of the fine particles. This is because the magnetic metal nanoparticles have the excellent dispersivity and high aspect ratio. Thus, the metal nanoparticles prepared in the present study have magnetic properties enough for the magnetic recording media application.

4. Conclusions

(1) The dependence of reaction rate constants in the formation of \( \alpha \)-FeOOH in the wet process and the crystallite size of \( (110) \) on Co content in \( \alpha \)-FeOOH has been made clear. Both the rate constants and crystallite size decrease with increasing Co contents. The zeta-potential of the formed \( \alpha \)-FeOOH particles changes from positive values to negative, and the negative potential increases slowly with increasing pH of the electrolytic solution. The negative potential of \( \alpha \)-FeOOH particles containing Co is larger than that without Co in the range of pH6–pH12.

(2) The relationships between the morphology of the formed \( \alpha \)-FeOOH particles and the cumulative distribution of particle size and the cobalt content have been investigated. The length of the major axis increases and the lengths of minor axes decrease with increasing Co content. Consequently, the aspect ratio increases remarkably. It is likely that \( \text{Fe(OH)}_2^+ \) complex ion precipitates preferentially on the c plane, and the particles grow remarkably in the direction of c axis. The interplanar spacing of the \( \alpha \)-FeOOH decreases with increasing Co content. When Co\(^{3+}\) ions are picked up into the crystal lattice to substitute with Fe\(^{3+}\) ions, the \( \alpha \)-FeOOH crystal lattice is strained by the compressive forces. Besides acicular \( \alpha \)-FeOOH particles, the cubical particles, Fe\(_2\)O\(_4\) of the spinel structure and/or Co ferrite substituted partially with Co\(^{3+}\) ion were observed for the case of Co content above 16 at%. The formed \( \alpha \)-FeOOH grew abnormally like whisker in the direction of major axis: c axis in the case of Co content more than 27 at%. The whisker-like nanoparticles were observed to grow with curving.

(3) The acicular magnetic metal nanoparticles were prepared from the \( \alpha \)-FeOOH nanoparticles through the dehydration and the hydrogen reduction. The metal nanoparticles of which the median diameters of major and minor axes were 130–290 nm and 22 nm, respectively, and the median aspect ratios were 6–13. The squareness ratio was as high as 0.89–0.91, in spite of the fine particles.

REFERENCES