Heterogeneously Junctioned Nano-Particles of Hematite and Goethite Formed in a Wet Process*

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Acicular α-FeOOH particles are formed through aging of ferric oxyhydroxide colloidal solution formed by the neutralization of FeCl₃ aqueous solution by NaOH. The effect of foreign ion addition to the colloidal solution on the formation and morphology of α-FeOOH particles has been investigated. The magnetic properties of Fe₂O₃ particles made from the obtained particles have also been investigated. The rate constant of the formation of α-FeOOH remarkably decreased, but the crystallite size of α-FeOOH particles increased with increasing the quantity of phosphate ion added even with small amounts. These results have been explained as follows: the phosphate ions are selectively adsorbed on the (a) plane of α-FeOOH, cover the (a) plane, and block the crystal growth of the (a) plane of the α-FeOOH. The quantities of the phosphate ion adsorbed on the b and c planes are relatively small. The complex ion of Fe(OH)₆⁻ is preferentially deposited on both (b) and (c) planes, and the crystal growth of (b) and (c) planes is greatly accelerated. The relationship between the morphology of the formed α-FeOOH particles and the quantity of phosphate ion added has been investigated. The asterisk type particles: α-FeOOH particles heterogeneously junctioned to α-Fe₂O₃ particles, were formed when a small amount of phosphate was added to the mother liquid. The α-FeOOH crystal epitaxially grew on the junction interface with the α-Fe₂O₃ crystal. In the case of the aging at the temperature as high as 80°C, the cross type junctioned particles were stably formed at pH below 12.0. The Fe₂O₃ particles with screw-like unique three-dimensional morphology were produced from the heterogeneously junctioned particles.

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1. Introduction

In the production process of magnetic recording media, acicular α-FeOOH particles are utilized as raw particles. Those particles are industrially 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 monodisperse 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). 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 crystalline α-FeOOH surface has been reported.¹⁻³ 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.⁴⁻⁹ However, those studies did not aim the shape control of α-FeOOH particles. On the other hand, as for shape control methods, many studies¹⁰⁻¹⁴ have been done on the effect of phosphate and sulfate ions on the morphology of α-Fe₂O₃ particles. Those studies pointed out that the phosphate and sulfate ions showed the peculiar adsorption mechanism.

In the present study, the effects of phosphate ion addition in the sol-gel-sol process on the formation rate and morphology of α-FeOOH particles have been investigated. Furthermore, the magnetic properties of Fe₂O₃ particles prepared from the obtained particles have also been examined.

2. Experimental Procedure

2.1 Sample preparation

A 0.075 kmol·m⁻³ FeCl₃ aqueous solution was prepared from a special grade reagent FeCl₃·6H₂O. A 0.469 kmol·m⁻³ NaOH solution was prepared from a special grade reagent NaOH. In addition, 0.8–20 mol·m⁻³ Na₃PO₄ solutions were also prepared from a special grade reagent Na₃PO₄. The FeCl₃ solution of 2.5 × 10⁻³ m³ and the NaOH solution in a predetermined quantity were mixed through a batch operation to obtain a mixed suspensions. The mixed suspensions were stirred in a homogenizer for 5 minutes and neutralized. Subsequently, the Na₃PO₄ solution in a predetermined quantity was added dropwise to the suspension, and a brown-red suspension was obtained at 22–24°C. The pH of the suspension was adjusted to 11.0–12.5. For comparison, the NaBO₂ in a predetermined quantity was added dropwise instead of Na₃PO₄. The FeCl₃ concentration of the suspensions was kept constant within the range of 0.038–0.041 kmol·m⁻³.

After the suspensions were aged in a thermal chamber at 55–80°C for 14–405 h, a 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 × 10² μS · m⁻¹, respectively. A CM-60S meter (TOA Electronics Inc.) and a platinum black electrode were used.
for the measurement of electrical conductivity. After the raffinate was dehydrated at 80°C for 12–24 h in a dryer and were ground to powder by a mortar, they were used as a sample for the further observation.

TG/DTA6300 and EXSTAR6000 thermal analysis system (Seiko Instruments Inc.) was used for the TG and DTA analysis. The formed particles were then dehydrated by heating at 673 K for 60 min in N2 and reduced at 653 K for 20–30 min in 20 mol%H2–80 mol%Ar. The obtained Fe2O4 particles were slowly oxidized to some extent at 318 K for 60 min in 1 mol%O2–99 mol%N2 to prevent the samples from ignition in atmosphere.

2.2 Measurements of powder properties

The formed particles were examined by a Fourier transform infrared spectroscopy (FT-IR), an X-ray diffraction powder method (XRD), a TEM observation and a selected-area electron diffraction (SAED) analysis. The samples for the FT-IR were prepared by a KBr tablet method. An infrared spectrophotometer JIR-6500 (JEOL) was used, and the infrared adsorption spectra were measured with a resolution of $4 \times 10^{-3}$ m$^{-1}$, within the wavenumber range of $500 \times 10^{2}$–$4000 \times 10^{2}$ m$^{-1}$. 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 CoKα. A crystalline size of the formed 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°. A JEM-200CX (JEOL) was used for the TEM observation and the SAED. 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. The magnetic properties of the formed Fe2O4 particles were also measured by VSM (Toei Kogyo Inc.) for the stamped sample with apparent density of $10^3$ kg m$^{-3}$ and with an external magnetic field of 400 kA m$^{-1}$.

3. Results and Discussions

3.1 Dependence of reaction rate and crystallite size on addition quantity of phosphate ion

The quantity of phosphate ion added to the colloidal mother liquid on the formation of α-FeOOH particles has been investigated. When the FeCl3 aqueous solution was neutralized by NaOH, amorphous ferric oxyhydroxide gel mother liquid of 0.040 kmol m$^{-3}$ FeCl3 and pH 12.0 was formed. After the addition of Na3PO4, the gel was aged at 55°C to grow α-FeOOH crystalline particles. The concentration of the α-FeOOH crystalline particles was evaluated from the absorbances of 3120 $\times 10^{2}$ m$^{-1}$ and 3380 $\times 10^{2}$ m$^{-1}$ of FT-IR spectrum, and plotted against the aging time in Fig. 1.

The quantity of phosphate ion added was varied in the range from 0 to 0.403 mol m$^{-3}$. Through aging the concentration of the α-FeOOH crystalline particles increased firstly, then approached a constant value. The increasing rate of the concentration of α-FeOOH crystalline particles obviously decreased with increasing addition quantity of phosphate ion.

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

$$\text{Fe}_3\text{O}_4(\text{OH})_{3-2x} \text{amor.} + x\text{H}_2\text{O} + \text{OH}^- \rightarrow \text{Fe(OH)}_4^- \quad (1)$$

$$\text{Fe(OH)}_4^- \rightarrow \alpha - \text{FeOOH(crys.)} + \text{H}_2\text{O} + \text{OH}^- \quad (2)$$

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

$$\text{Fe}_3\text{O}_4(\text{OH})_{3-2x} \text{amor.} \rightarrow \alpha - \text{FeOOH(crys.)} + (1 - x)\text{H}_2\text{O} \quad (3)$$

When the unstable amorphous ferric oxyhydroxide is dissolved into the colloidal solution, the complex ion Fe(OH)$_4^-$ is formed. Then, the α-FeOOH crystalline particles are precipitated when the concentration of the complex ions are supersaturated.

The rate equation of a primary reaction as shown in eq. (4) can be applicable to the formation reaction of α-FeOOH crystalline particles.\textsuperscript{15-20}

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

The results shown in Fig. 1 were analyzed by the reaction rate equation of 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 the quantity of anions added to the mother liquid, and shown in Fig. 3. The results of carbonate ion and borate ion as well as phosphate ion are shown for comparison in the same figure. The rate constant remarkably decreases with increasing the quantity of phosphate ion added to the mother liquid. The rate also decreased in the case of borate ion. On the other hand, in the case of carbonate ion it slightly decreased. Particularly in the case of phosphate ion, the decrease of the rate constant is the largest even with small amounts of $10^{-3}$ times as small as the case of borate ion and carbonate ion.

The crystallite size of α-FeOOH particles was calculated from the full width at half maximum (FWHM) of the 110 reflection of the α-FeOOH particles by applying a Scherrer’s equation shown in eq. (5).
where $D_{\text{hkl}}$, $\beta$, $\theta$, and $\lambda$ are the mean crystallite size, the FWHM, the Bragg angle and the wavelength 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 the quantity of anions added to the mother liquid is shown in Fig. 4. In the case of phosphate ion, the crystallite size increases with increasing the addition quantity even with small amounts. It also increases in the case of borate ion. On the other hand, the crystallite size slightly decreases in the case of carbonate ion.

The morphology of the $\alpha$-FeOOH particles obtained was observed by TEM. The distribution of the particle sizes was calculated from the statistical analysis of TEM photographs. The cumulative distributions of the length of major and minor axes and the aspect ratio of the acicular $\alpha$-FeOOH particles were analyzed, and plotted against the addition quantity of phosphate ion in the mother liquid, as shown in Fig. 5. Both the lengths of the major and minor axes increase with increasing the quantity of phosphate ion added, but the aspect ratio was almost constant. As shown in the figure, the shape of $\alpha$-FeOOH particles changes from needle to plate with increasing the quantity of phosphate ion added. This may be because the crystal growth proceeds in the directions of $(b)$ and $(c)$ axes, but it is blocked in the directions of $(a)$ axis.
According to the previous studies\(^1\)\(^-\)\(^5\) about the adsorption of anions on \(\alpha\)-FeOOH, H\(_3\)PO\(_4\)\(^-\) or HPO\(_4\)\(^2-\) and SO\(_4\)\(^2-\) ions exchange-adsorb with two OH\(^-\) on the (100) plane of \(\alpha\)-FeOOH. The CO\(_3\)\(^2-\) chemically binds with O\(^2-\) on \(\alpha\)-FeOOH. A similar adsorption mechanism of phosphate ion can also explain the results of the present study in the following manner. The quantity of H\(_3\)PO\(_4\)\(^-\) or HPO\(_4\)\(^2-\) adsorbed on the crystal surface of \(\alpha\)-FeOOH increases with increasing phosphate ion concentration in the colloidal mother liquid. The phosphate ion would be selectively adsorbed on the (a) plane of \(\alpha\)-FeOOH. In consequence, the formation rate of \(\alpha\)-FeOOH remarkably decreases even with a small amount of phosphate added, because the crystal growth of the (a) plane in \(\alpha\)-FeOOH is blocked. On the other hand, the quantity of H\(_2\)PO\(_4\)\(^-\) or HPO\(_4\)\(^3-\) adsorbed on the (c) and (b) planes is relatively small. The complex ion of Fe(OH)\(_4\)\(^-\) preferentially deposited on the (c) and (b) planes, and consequently, the crystal growth of their planes is greatly accelerated. Therefore, the shape of \(\alpha\)-FeOOH particles seemingly changes from the needle to the plate form; that is long both in major and minor axes, but is thin in the thickness direction. Consequently, the major and minor axes increase as well as the crystallite size in the (110) direction with increasing the quantity of phosphate ion added.

As shown in Fig. 3, the behaviour of the borate ion addition is similar to that of phosphate ion. This suggests that the mechanism similar to the phosphate ion addition is expected to the borate ion addition. However, there found a difference in the concentrations of the additives. The same effect for the phosphate ion addition is observed at the borate concentration as high as 10\(^3\) times of phosphate ion. This is presumably caused by a difference in valence between borate ion and phosphate ion. That is to say, the electrostatic interaction between \(\alpha\)-FeOOH surface and phosphate ion is larger than that of borate ion. On the other hand, as shown in Fig. 3, the behavior of the carbonate ion differs from those of phosphate and borate ions. This suggests that the selective adsorption of carbonate ions might be much weaker than the other two ions.

### 3.2 Effect of addition of phosphate ion on the morphology of formed particles

The shape of the particles was observed by TEM. Figure 6 shows the particles formed at various amounts of phosphate ion added to mother liquids. As clearly shown in Fig. 6, the shape of the formed particles changes from needle to thin plate grown in the direction of the major and minor axes. Asterisk type particles were formed when phosphate ion was added. Furthermore, in the region of large amounts of addition, ultra fine particles were formed. The relationship between the XRD patterns of the formed particles and the quantity of phosphate ion added to the mother liquid is also shown in Fig. 7. Among the formed particles, not only \(\alpha\)-FeOOH but also a slight amount of \(\alpha\)-Fe\(_2\)O\(_3\) were detected, and the amount of \(\alpha\)-Fe\(_2\)O\(_3\) increases with increasing the quantity of phosphate ion added. In the region of large quantities of addition, the growth of \(\alpha\)-FeOOH is blocked at an early stage.

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Fig. 6 Relationship between morphology of formed particles and quantity of phosphate ion added to mother liquid: (a) without addition, (b) 0.241 mol·m\(^{-2}\), (c) 0.638 mol·m\(^{-2}\), (d) 1.018 mol·m\(^{-2}\). FeCl\(_3\) concentration, pH and aging temperature of mother liquid are 0.039-0.041 kmol·m\(^{-3}\), 12.0 and 55°C, respectively.
The TEM image and electron diffraction patterns of the asterisk type particle are shown in Fig. 8. An over-all electron diffraction pattern of the asterisk type particle shows the presence of $\alpha$-Fe$_2$O$_3$ mixed with $\alpha$-FeOOH. In Fig. 8, the SAED patterns of A through F of the asterisk type particle are shown. The SAED patterns of A through F show only orthorhombic patterns from $\alpha$-FeOOH. Based on these results, we can conclude that an hexagonal $\alpha$-Fe$_2$O$_3$ is formed in the center of the asterisk type particle. The (a) and (b) axes of the hexagonal $\alpha$-Fe$_2$O$_3$ are graphically illustrated in Fig. 8, and the (c) axis is vertical to the (a) and (b) axes. Furthermore, the major and minor axes of $\alpha$-FeOOH plate particles shown as A to F are the (c) and (b) axes, respectively, and (a) axis is vertical to the (c) and (b) axes. The angle in which the six pieces of $\alpha$-FeOOH particles intersect is 60 degrees. The TEM observation with the sample holder tilted revealed that the several $\alpha$-FeOOH particles overlapped at regular intervals in the direction of (c) axis of $\alpha$-Fe$_2$O$_3$. The same results were obtained also in the SEM observation. As mentioned above, the asterisk type particle has the morphology in which an $\alpha$-Fe$_2$O$_3$ particle is positioned in the center of the asterisk, and the several $\alpha$-FeOOH particles are joined to the side planes parallel to the (c) axis of the $\alpha$-Fe$_2$O$_3$ particle. Such morphology is usually known as heterogeneous junction. Because the interplanar spacings of [0006] and [1120] in $\alpha$-Fe$_2$O$_3$ are very close to those of (002), (061) and (040), (021) in $\alpha$-FeOOH respectively, the $\alpha$-FeOOH crystal may epitaxially have grown on the junction interface with the $\alpha$-Fe$_2$O$_3$ crystal. According to the JCPDS data, the interplanar spacings of the (0006) and (1120) of $\alpha$-Fe$_2$O$_3$, are 229.2 pm and 251.9 pm, respectively. On the other hand, the interplanar spacings of (200) in the (a) axis, and (040) in the (b) axis of the $\alpha$-FeOOH are 230.3 pm and 249.9 pm, respectively. The spacings of the (0006) of $\alpha$-Fe$_2$O$_3$ and (200) of $\alpha$-FeOOH are very close to each other. The spacings of (1120) of $\alpha$-Fe$_2$O$_3$ and (040) of $\alpha$-FeOOH are also close enough to allow epitaxial growth. Based on the above results, a schematic view of the asterisk type fine particle is shown in Fig. 9. Atkinson et al. reported that $\alpha$-FeOOH twin crystals epitaxially grew on an $\alpha$-Fe$_2$O$_3$ nuclei, because the interplanar spacings of the $\alpha$-FeOOH are approximately equal to that of the $\alpha$-Fe$_2$O$_3$. Bailey et al. also reported on the formation of star-shaped particles of $\beta$-FeOOH. However, the asterisk type heterogeneous junctioned particles have been found firstly in the present study. The mechanism of the formation of the asterisk type particle, in which $\alpha$-FeOOH and $\alpha$-Fe$_2$O$_3$ are junctioned heterogeneously, can be explained in the following manner. In high pH region, $\alpha$-FeOOH is usually dominant in nucleation and growth. But by the addition of phosphate, the nucleation and growth of $\alpha$-FeOOH were depressed, and the formation of the $\alpha$-Fe$_2$O$_3$ can compete with that of the $\alpha$-FeOOH though the growth rate was slow. There-
fore, simultaneous nucleation of $\alpha$-FeOOH and $\alpha$-Fe$_2$O$_3$ may occur, and several $\alpha$-FeOOH crystals nucleate heterogeneously on the surfaces of $\alpha$-Fe$_2$O$_3$ using them as the seed, and grow outwardly.

The relationship between the morphology of heterogeneously junctioned particles (HIP) and the pH of the mother liquid is shown in Fig. 10. The $\alpha$-Fe$_2$O$_3$ positioned in the center of the asterisk grows significantly in the direction of the (c) axis in the low pH region of 11.0, whereas the $\alpha$-FeOOH is shortened in the direction of the (c) axis. At the same time, the number of $\alpha$-FeOOH particles junctioned to the central $\alpha$-Fe$_2$O$_3$ stem increases.

The effect of the aging temperature on the morphology of heterogeneously junctioned particles has also been investigated by TEM. Figure 11 shows the relationship between the morphology of the junctioned particles and the pH of mother liquid in the case of aging at 80°C. Both coarser plate and fine acicular $\alpha$-FeOOH particles are produced only in the high pH region of 12.5. Junctioned particles are little observed under these conditions. However, isolated plate and acicular $\alpha$-FeOOH particles disappear with decreasing pH. The junctioned particles are stably produced at pH below 12.0. Those junctioned particles are different from the asterisk type particles described above, and have a morphology in which about two pieces of $\alpha$-FeOOH are joined to the stem of $\alpha$-Fe$_2$O$_3$. Particularly, the $\alpha$-Fe$_2$O$_3$ grows remarkably in the direction of the (c) axis. The $\alpha$-Fe$_2$O$_3$ in the junctioned particles changes to the slender shape with decreasing pH as it shrinks in the direction of the minor axis. On the other hand, the plates of $\alpha$-FeOOH are blocked to grow, and are shortened. The rela-

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Fig. 9 Schematic view of asterisk type fine particle joined heterogeneously with $\alpha$-Fe$_2$O$_3$ and $\alpha$-FeOOH: (a) sketch of particle in the c axis direction of $\alpha$-Fe$_2$O$_3$, (b) sketch of particle in the c axis direction of $\alpha$-FeOOH.

Fig. 10 Relationship between morphology of heterogeneously junctioned particles and pH of mother liquid: (a) and (c) are pH 11.0, (b) and (d) are pH 12.0. Quantity of phosphate ion added, FeCl$_3$ concentration and aging temperature of mother liquid are 0.38–0.39 mol m$^{-3}$, 0.039 kmol m$^{-3}$ and 55°C, respectively.
3.3 Preparation of Fe₂O₄ particles made from heterogeneously junctioned particles

The HJP of α-Fe₂O₃ and α-FeOOH were dehydrated at 673 K for 60 min to obtain α-Fe₂O₃, and then reduced to Fe₂O₃ by hydrogen. The TEM images and the SAED patterns of the asterisk type particles are shown in Fig. 14. The asterisk type HJP of α-Fe₂O₃ and α-FeOOH is shown in Fig. 14(a). The formed particles shown in Fig. 14(b) were prepared by the dehydration of the HJP shown in Fig. 14(a) at
Fig. 13  TEM images and selected-area electron diffraction patterns of heterogeneously junctioned particle: (a) and (c) are α-Fe$_2$O$_3$, (b) and (d) are α-FeOOH. Quantity of phosphate ion added, FeCl$_3$ concentration and pH of mother liquid are 0.39 mol·m$^{-3}$, 0.039 kmol·m$^{-3}$ and 11.5, respectively, and aging temperature is 80°C.

673 K in N$_2$. Furthermore, the formed particles shown in Fig. 14(c) were prepared by the reduction of the α-Fe$_2$O$_3$ particles shown in Fig. 14(b) at 653 K in a 20 mol%H$_2$–80 mol%Ar mixture. It was confirmed by SAED that the particles shown in Fig. 14(a) contain α-FeOOH and α-Fe$_2$O$_3$, and that the ones shown in Fig. 14(b) and Fig. 14(c) contain α-Fe$_2$O$_3$ and Fe$_3$O$_4$, respectively. It was found that the α-Fe$_2$O$_3$ and Fe$_3$O$_4$ particles retain the original morphology of the precursor; asterisk type particles.

The TEM images and the SAED patterns of the HJP and their dehydrated and reduced particles are shown in Fig. 15. The HJP of α-Fe$_2$O$_3$ and α-FeOOH are shown in Fig. 15(a). The conditions of dehydration and reduction of the HJP are similar to those of Fig. 14. Figure 15(a) shows the diffraction patterns of α-FeOOH and α-Fe$_2$O$_3$, Fig. 15(b) and Fig. 15(c) show the diffraction patterns of α-Fe$_2$O$_3$ and Fe$_3$O$_4$, respectively. It is similar to the case of Fig. 14 in which the α-Fe$_2$O$_3$ and Fe$_3$O$_4$ particles retain the original morphology of the precursor HJP.

The magnetic properties of the Fe$_3$O$_4$ particles produced from the asterisk type particles and the cross type particles are shown in Table 1. In either case, both saturation magnetization and coercivity are slightly small in comparison with the magnetic particles conventionally used for the production of recording media. This may be caused by a number of nano-size pores formed in the Fe$_3$O$_4$ during dehydration. As described above, the magnetic Fe$_3$O$_4$ particles with screw-like unique three-dimensional morphology can be produced.

Fig. 14  TEM images and SAED patterns of the asterisk type formed particles: (a) heterogeneously junctioned particle of α-Fe$_2$O$_3$ and α-FeOOH crystals, (b) α-Fe$_2$O$_3$ particle prepared by the dehydration of the heterogeneously junctioned particle, (c) Fe$_3$O$_4$ particle prepared by the reduction of the α-Fe$_2$O$_3$ particle, (d) SAED pattern of (a) particle, (e) SAED pattern of (b) particle, (f) SAED pattern of (c) particle. Quantity of phosphate ion added, FeCl$_3$ concentration and pH of mother liquid are 0.638 mol·m$^{-3}$, 0.040 kmol·m$^{-3}$ and 12.0, respectively, and aging temperature is 55°C.

4. Conclusions

(1) The dependencies of reaction rate constants in the formation of α-FeOOH and the α-FeOOH crystallite size on the quantity of phosphate ion added to the mother liquid have been made clear. The rate constant remarkably decreases, but the crystallite size increases with increasing the quantity of phosphate ion added even with small amounts. The phosphate ion is selectively adsorbed on the (a) plane of α-FeOOH, and the reaction rate remarkably decreases because the crystal growth of the (a) plane in the α-FeOOH is blocked by covering the phosphate ion. On the other hand, the quantity of the phosphate ion adsorbed on the (b) and (c) planes is relatively small. As a result, the complex ion of Fe(OH)$_4$ is preferentially deposited on both the planes, and the crystal growth of their planes is greatly accelerated. Therefore, it can be considered that the shape of α-FeOOH particles changes to a plate form that is large in the length of the major and minor
FeOOH particles heterogeneously junctioned to $\alpha$-Fe$_3$O$_4$ particles, were formed when a small amount of phosphate was added to the mother liquid. The $\alpha$-FeOOH crystal epitaxially grows on the junction interface with the $\alpha$-Fe$_3$O$_4$ crystal. The $\alpha$-Fe$_3$O$_4$ positioned in the center of the asterisk grows significantly in the direction of the (c) axis in the low pH region of the mother liquid of pH 11.0, while the $\alpha$-FeOOH is shortened in the direction of the (c) axis. Further, in the case of the aging at a high temperature of 80°C, the cross type junctioned particles are stably produced below pH 12.0. Those cross type junctioned particles have the morphology in which about two pieces of $\alpha$-FeOOH are joined to the stem of $\alpha$-Fe$_3$O$_4$. Particularly, the $\alpha$-Fe$_3$O$_4$ grows remarkably in the direction of the (c) axis.

(3) The $\alpha$-Fe$_3$O$_4$ particles with screw-like unique three-dimensional morphology can be produced from the heterogeneously junctioned particles by dehydration and reduction processes.

REFERENCES