JOURNAL OF MATERIALS SCIENCE 28 (1993) 5247–5250

Hydrothermal synthesis of barium ferrite fine particles from goethite

H. KUMAZAWA, H.-M. CHO, E. SADA
Department of Chemical Engineering, Kyoto University, Kyoto 606–01, Japan

Barium ferrite fine particles were prepared from aqueous suspensions containing goethite (α–FeOOH) and barium hydroxide by a hydrothermal method. Barium ferrite particles of thin hexagonal plate shape could be produced from commercially available goethite with an Fe:Ba molar ratio of 7.2, whereas barium ferrite particles could be produced from synthesized goethite with a molar ratio of unity. The effects on the size of hexagonal platelike particles of such reaction conditions as temperature, stirring speed and alkali concentration were investigated. Particles of 0.6 to 0.8 μm mean size were prepared under the reaction conditions covered here.

1. Introduction

Barium ferrite has been widely used as a permanent magnet because of its high magnetization and coercivity. Recently, ultrafine barium ferrite particles of hexagonal plate shape have been used as the solid material for coated perpendicular magnetic recording media. In our preceding work [1], ultrafine particles of barium ferrite were synthesized from an aqueous mixed solution of ferric nitrate and barium nitrate by a hydrothermal method. The relations of the particle size and shape to such operating variables as alkali concentration, stirring speed in the autoclave, hydrothermal temperature and time were investigated systematically and a mechanism of particle growth was proposed. The operating conditions were determined to form ultrafine particles of thin hexagonal plate shape less than 0.1 μm in size which were suitable for use in perpendicular magnetic recording media.

It has been reported that in the formation of barium ferrite under hydrothermal conditions, goethite (α-FeOOH) is an intermediate species [2]. Hence, barium ferrite may also be synthesized by the hydrothermal treatment of an aqueous suspension containing goethite and barium ion. In this case, the reaction sequence leading to barium ferrite then becomes shorter than the hydrothermal treatment of an aqueous mixed solution of ferric nitrate and barium nitrate. A shorter reaction sequence may be more favourable for the control of particle size and shape or for the formation of fine particles with a narrow size distribution.

In the present work, barium ferrite fine particles were prepared from an aqueous suspension containing goethite and barium hydroxide by the hydrothermal method. As in the case of barium nitrate and ferric nitrate, the relation between the particle size and the reaction conditions was examined systematically. Comparison with the findings on hydrothermal synthesis of the same particles from a mixed solution of ferric nitrate and barium nitrate [1] allowed a mechanism of particle formation to be deduced.

2. Experimental procedure

A stainless steel autoclave (Nitto, UN-4) equipped with a stirrer (Nitto, NS-8) was employed for hydrothermal synthesis of barium ferrite particles. The internal diameter and height of the autoclave are 4.6 and 14.0 cm, respectively. The stirrer is of the paddle type. The length and width of the paddle are 3.0 and 1.2 cm, respectively. The volume of the starting slurry containing goethite and barium ion, is 50 cm^3 and the slurry is fed into a pot made of titanium, whose diameter and height are 3.8 and 10.8 cm, respectively. Goethite (4.45 g) is added to the slurry. Two kinds of goethite were used: a commercially available one whose mean size was 1 μm and a synthesized one of 0.2 μm mean size. The concentrations of barium hydroxide were fixed at 0.14 and 1.0 mol dm^{-3}, respectively, when commercial and synthesized goethite particles were used. Thus, the molar ratio of Fe to Ba in a starting slurry was fixed at 7.2 and 1.0, respectively, for these two kinds of goethite particles. The hydrothermal temperature ranged from 200 to 300 °C. The heating rate to a specified hydrothermal temperature was 4 °C min^{-1}. The stirring speed in the autoclave was varied up to 500 r.p.m. The hydrothermal treatment was continued for 20 h.

Prepared fine particles were rinsed with distilled water several times, and dried at around 100 °C in an oven. Afterwards, the particles were observed by means of a scanning electron microscope (SEM) (Hitachi S-510) to permit assessment of particle shape and size. Some of the samples were examined by X-ray powder diffraction (Shimazu XD-610 and Rigaku Denki RAD-B).

3. Results and discussion

First, an aqueous slurry of commercially available goethite particles was treated hydrothermally at a temperature of 300 °C for a period of 5 h. The volume of the starting slurry was 50 cm^3 and it contained 4.45 g of goethite particles. From scanning electron micrographs the particles were found to be thin and plate-like, about 0.3 μm in mean size. X-ray diffraction revealed that the material was crystalline α-Fe_2O_3. Under hydrothermal conditions, α-FeOOH is dehydrated to form α-Fe_2O_3. Presumably the product is formed by the dissolution of α-FeOOH, followed by crystallization of α-Fe_2O_3. The dehydration rate is presumed to depend on the particle size, so the dehydration rate may increase with increasing outer surface area of particles. The barium ferrite particle may be formed by incorporation of barium ion under such hydrothermal conditions that α-FeOOH is dehydrated to form α-Fe_2O_3. Similarly, the barium ferrite particle is formed by dissolution followed by crystallization.

Fig. 1 shows a scanning electron micrograph of barium ferrite particles. Commercial goethite particles with mean size of 1 μm were used as Fe source. The starting slurry contained Fe and Ba with a molar ratio of 7.2, though the molar ratio was equal to 12 from the stoichiometry of the overall reaction

$$12FeOOH + Ba(OH)_2 \rightarrow BaO{\cdot}6Fe_2O_3 + 7H_2O \quad (1)$$

The particles were found to be thin, hexagonal and plate-like in shape. The X-ray diffraction pattern of this sample is shown in Fig. 2, which is in complete agreement with the standard pattern of barium ferrite. No α-Fe_2O_3 was formed under these conditions. Fig. 3 shows the cumulative size distribution curve of this sample plotted on log–probability paper. From the graph, the median size (50% size) and the geometric standard deviation defined as the ratio of 84.1% size to 50% size are determined to be 0.73 μm and 1.52, respectively. The same figure presents the cumulative size distribution curve for barium ferrite particles synthesized hydrothermally from a mixed solution of ferric nitrate and barium nitrate at 300 °C [1]. The geometric standard deviation in this case was 1.61, a little bit larger than that of the material prepared from a slurry containing commercial goethite and barium hydroxide (1.52).

Barium ferrite particles were prepared at different temperatures ranging from 225 to 300 °C at a constant stirring speed of 200 r.p.m. The hydrothermal treatment period was fixed at 5 h. The mean particle size is plotted against temperature as closed circles in Fig. 4. The particle size is shown to decrease with rising treatment temperature. The time dependence of particle size is shown as closed circles in Fig. 5, where barium ferrite particles were produced at a constant temperature of 300 °C and a constant stirring speed of 200 r.p.m. The product after a short hydrothermal treatment at 300 °C was identified as barium ferrite from its X-ray powder diffraction pattern. No α-Fe_2O_3 was formed even in short treatment times. Presumably no direct transformation such as α-$Fe_2O_3 \rightarrow BaO{\cdot}6Fe_2O_3$ takes place, though Barb *et al.* [3] have reported that the appearence of $BaO{\cdot}6Fe_2O_3$ in the hydrothermal process is preceded

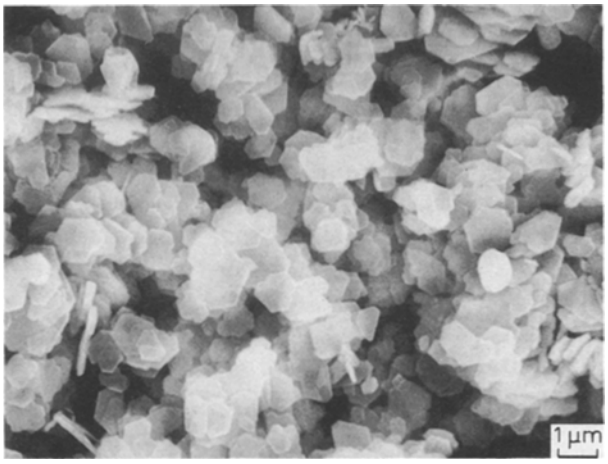

Figure 1 Scanning electron micrograph of barium ferrite particles prepared by hydrothermal treatment at 300 °C and a stirring speed of 200 r.p.m. for 5 h.

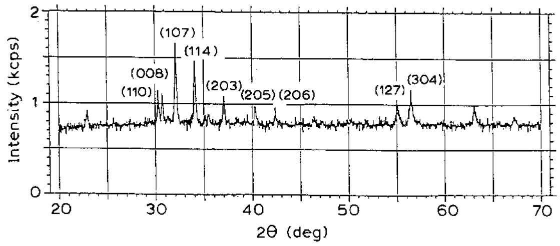

Figure 2 X-ray diffraction pattern of barium ferrite particles synthesized by hydrothermal treatment at 300 °C and a stirring speed of 200 r.p.m. for 5 h.

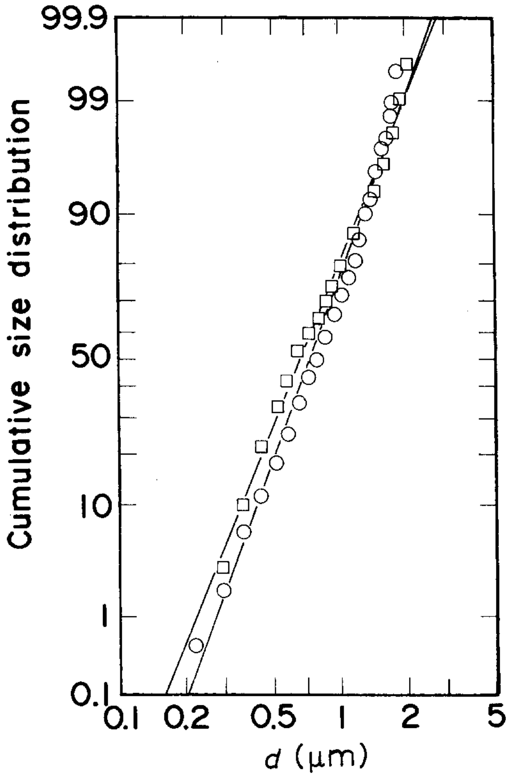

Figure 3 Cumulative size distribution of barium ferrite particles from (○) commercial goethite and (□) ferric nitrate as Fe source.

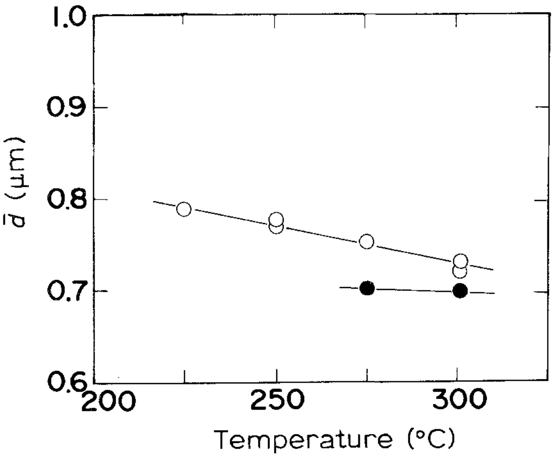

Figure 4 Dependence on temperature of mean size of barium ferrite particles synthesized from (○) commercially available and (●) prepared goethite particles, with stirring at 200 r.p.m. for 5 h.

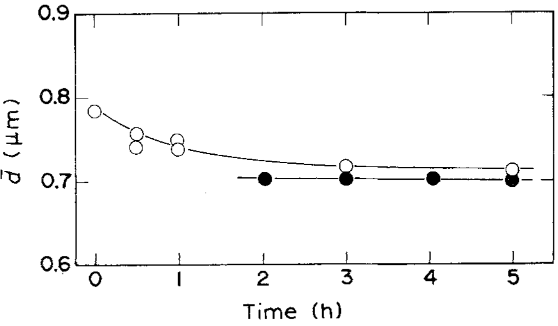

Figure 5 Time dependence of mean size of barium ferrite particles synthesized at 300 °C from (○) commercially available and (●) prepared goethite particles, with stirring at 200 r.p.m.

by the formation of an α-Fe_2O_3 phase. The particle size gradually decreased with increasing treatment time and approached a constant value. The dependence of the mean size $\bar{d}$ on time t can be expressed as

$$\frac{\bar{d} - \bar{d}_\infty}{\bar{d}_0 - \bar{d}_\infty} = \exp(-kt) \qquad (2)$$

where $\bar{d}_0$ and $\bar{d}_\infty$ refer to the mean particle sizes in the limits of treatment time zero and infinity, respectively. In this example, $\bar{d}_0$ and $\bar{d}_\infty$ are estimated to be 0.78 and 0.71 μm, respectively, and k is determined to be 1.0 h^{-1} at 300 °C. The decrease in the mean particle size apparently follows a first-order kinetic law. The decrease in the particle size with increasing treatment time may be caused by an increase in the packing density of atoms in the crystals or by increasing crystallinity, as has been observed in the hydrothermal synthesis of hydroxyapatite ultra-fine particle [4].

It is judged from Figs 4 and 5 that in the course of a rise in temperature to 300 °C, α-FeOOH is transformed into barium ferrite and that during the hydrothermal treatment at a constant temperature of 300 °C, the crystallinity of precipitated particles increases. The trend that the particle size decreases with rising temperature and increasing treatment time is in contrast with experimental evidence that in the hydrothermal synthesis of the same particles from a mixed solution of ferric nitrate and barium nitrate, particles grow presumably by Ostwald ripening [1].

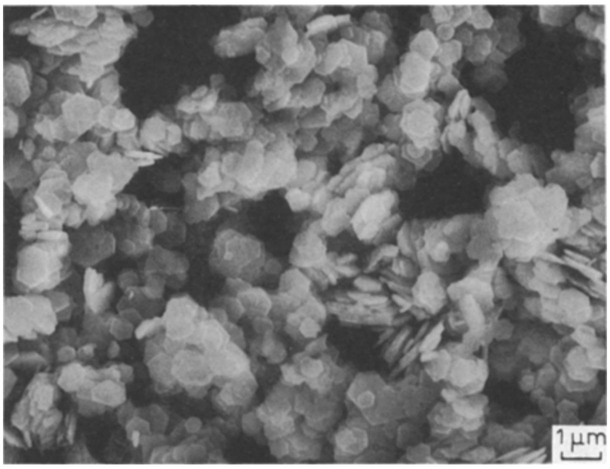

Figure 6 Scanning electron micrograph of barium ferrite particles synthesized from prepared goethite with a molar ratio of Fe to Ba fixed at unity.

The open circles in Figs 4 and 5 represent the data taken from commercially available α-FeOOH particles as Fe source. The particles have 1 μm mean size and a wide size distribution. Next, similar experimental results will be described in which extremely fine α-FeOOH particles synthesized by air oxidation of aqueous alkaline suspensions of $Fe(OH)_2$ [5] were employed as the starting material. The mean size and geometric standard deviation of log–normal distribution were 0.2 μm and 1.2, respectively.

An SEM image of barium ferrite particles synthesized in this way is demonstrated in Fig. 6. Barium ferrite particles could be produced only when the molar ratio of Fe to Ba in a starting slurry was fixed at unity, though barium ferrite could be prepared at the molar ratio of 7.2 when 1 μm commercial α-FeOOH particles were used. The particles prepared are also of thin hexagonal plate-like shape, and the cumulative size distribution can be described in terms of a log–probability function. From the plots on log–probability paper the median and the geometric standard deviation were determined to be 0.7 μm and 1.44, respectively. The X-ray diffraction pattern of particles formed at the molar ratio of unity is demonstrated in Fig. 7a, which completely agrees with the standard pattern of barium ferrite. Fig. 7b shows the X-ray diffraction pattern of particles formed at the molar ratio of 7.2. The inter lattice distance at around 30° of 2θ is not distinctly defined. The specific outer surface area of synthesized α-FeOOH whose size is 0.2 μm is much larger than that of commercial α-FeOOH particles of 1 μm. Consequently, the dehydration rate for synthesized α-FeOOH is much greater than that for commercial material. There must be a balance between the incorporation of barium ion into the barium ferrite crystal and the dehydration of α-FeOOH. Therefore, as the size of α-FeOOH particle decreases, the molar ratio of Fe to Ba must be decreased.

The mean size of barium ferrite particles prepared from synthesized α-FeOOH particles was plotted against treatment temperature as closed circles in Fig. 4. The particles are only slightly smaller than

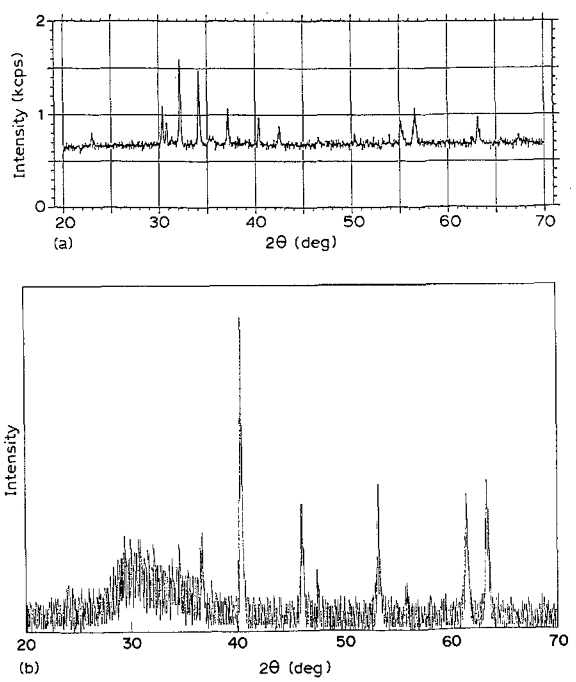

Figure 7 X-ray diffraction patterns of particles formed at the molar ratio of Fe to Ba to (a) unity and (b) 7.2.

those prepared from commercial α-FeOOH. The variation of particle size with treatment time is shown as closed circles in Fig. 5. Well-crystallized barium ferrite particles formed only after 2 h of treatment.

When barium ferrite particles were synthesized hydrothermally from aqueous mixed solutions of ferric nitrate and barium nitrate, the particle size decreased with an increase in alkali molar ratio defined as $[OH^-]/[NO_3^-]$ [1]. Particles about 0.1 μm in size were produced at molar ratios above 6. In the preparation of the same particles from α-FeOOH, addition of alkali may also possibly result in a decrease in particles size. As the concentration of NaOH increased, the mean size decreased, but unfortunately the ultrafine particles of about 0.1 μm could not be formed. The influence of stirring speed on the particle size was investigated for barium ferrite prepared from commercial α-FeOOH particles. The mean size decreased only slightly with increasing stirring speed. Such experimental evidence may support the concept that during hydrothermal treatment at a constant temperature (e.g. 300 °C), an increase in the crystallinity of precipitated particles mainly proceeds instead of particle growth driven by Ostwald ripening.

References

1. E. SADA, H. KUMAZAWA and H. -M. CHO, *Ind. Eng. Chem. Res.* **30** (1991) 1319.
2. M. KIYAMA, *Bull. Chem. Soc. Jpn* **49** (1976) 1885.
3. D. BARB, L. DIAMANDESCU, A. RUCCI, D. TARABASANU-MIHAILA and V. TEODORESCU, *J. Mater. Sci.* **21** (1986) 1118.
4. E. SADA, H. KUMAZAWA and Y. MURAKAMI, *Chem. Eng. Commun.* **103** (1991) 57.
5. E. SADA, H. KUMAZAWA, K. MAKINO and H. -M. CHO, *ibid.* **91** (1990) 225.

Received 17 March 1992
and accepted 24 February 1993