Korean J. Chem. Eng., **21**(3), 582-588 (2004)

Characterization of Barium Hexaferrite Produced by Varying the Reaction Parameters at the Mixing-Points in a Supercritical Water Crystallization Process

Sung-Chan Nam† and Gun-Joong Kim*

Korea Institute of Energy Research, P.O. Box 103, Yusong, Daejeon 305-600, Korea
*Inha University, #253 YongHyun-dong, Nam-Ku, Incheon 402-751, Korea
(*Received 4 September 2003 • accepted 30 December 2003*)

Abstract–Barium hexaferrite ($BaFe_{12}O_{19}$) was synthesized from a $Ba(NO_3)_2$, $Fe(NO_3)_3$ and KOH mixed solution by hydrothermal treatment of the solution using a supercritical water flow apparatus. The first step is the hydrolysis of the nitrates of barium and iron in potassium hydroxide; the pressure and temperature were adjusted in the respective range of 25-40 MPa and 100-250 °C in tee reactor (MP2). The second one is the dehydration of the formed hydrolytic products, under the supercritical state of the solvent in the range of 25-40 MPa, 300-450 °C and 40-100 s in tubular flow reactor (MP3). All samples of barium hexaferrite were prepared without calcination of the dehydrated products. Using this method, smaller, uniform-size and single-phase $BaFe_{12}O_{19}$ nanocrystals could be easily obtained.

Key words: Continuous, Mixing Point, Barium Hexaferrite, Reaction Parameter

INTRODUCTION

Barium hexaferrite has the formulation of $BaO \cdot 6Fe_2O_3$ and shares the same hexagonal crystal structure as that of magentoplumbite. It is known that the substance is prone to plate formation as its c-axis growth is restricted and it tends to primarily grow in the basal plane. The resulting crystal, therefore, shows the hexagonal, plate-like structure, and high-density recording is possible through perpendicular magnetic recording as the easy-direction of magnetization is formed perpendicular to the plate plane. Also, the substance is chemically stable and has high electric resistance (~10^6 Ωcm) and Curie temperature, minimizing the loss of stored data after prolonged storage. Therefore, it has gained attention as a high-density magnetic and magneto-optic recording medium for the next-generation HDTV recording tapes and computer-related storage systems [Fujiwaral, 1985]. In order for it to be used as a high-density magnetic recording medium, however, there are delicate conditions that have to be satisfied: the formed particles must be evenly fine in size and have high dispersion in an organic matter. The substance, therefore, cannot be synthesized in the conventional ceramic routes and a new process is required.

The conventional hydrothermal method is a process where the aqueous solution or slurry of the metal salt is hydrothermally treated and the resulting product is hydrolyzed into the hydroxide precipitation. The simple process offers high crystallinity and good uniformity of particle size. However, it requires long reaction times and has low productivity due to the batch type hydrothermal process [Sada et al., 1991; Kumazawa et al., 1995].

On the other hand, the synthesis in supercritical water is based on uniform nucleus formation and supersaturation. As the particle size decreases with an increase in the supersaturation, control of thermodynamic property and mass transfer characteristics is easy with minute changes in temperatures and/or pressures in the supercritical conditions. If the optimum conditions are selected, the particle size changes from the micron to the nanometer range, with an increase in the supersaturation. Depending on the concentration of the solution and residence time, the growth direction and shapes of the crystallized particles, particle size and distribution of particle sizes may be easily controlled.

When the metal oxides are synthesized from aqueous solution of metal salt with the use of supercritical water crystallization, the reaction seems to go through a two stage reaction: hydrolysis and dehydration.

$$\text{Step 1. } M(NO_3)_x + xH_2O = M(OH)_x + xHNO_3 \quad (1)$$

$$\text{Step 2. } M(OH)_x = MO_{x/2} + x/2H_2O \quad (2)$$

where M is the metal. In a comparison between the conventional hydrothermal synthesis method and this proposed process, when the precursors are metal nitrate and hydroxide, hydrolysis is very speedy in both processes but dehydration is relatively slow in the conventional hydrothermal synthesis method as it takes places on the surface of the hydrous oxide particles. In the proposed process, dehydration is faster because of the use of high-temperature, supercritical water, which speeds up particle formation [Hakuda et al., 1998; Rho, 2002].

In particular, Hakuda et al. [1998] studied the reaction mechanism of barium ferrite in the batch and flow apparatus when the concentration and residence time were changed at 30 MPa, 400 °C. In conclusion, uniform barium ferrite of size 0.1-0.2 μm was obtained at $Fe(NO_3)_3$=0.05 M, Ba : Fe=0.05, and R=4.

Nevertheless, details of inorganic crystallization using supercritical water are not well known. Especially, there has been no study verifying the changes in the morphology and size of the particles depending on the conditions at the mixing-points in the continuous synthesis process for barium hexaferrite. In this study, therefore, we assume that the seed products created in the 1st stage hydrolytic reaction in the metal nitrate aqueous solution and hydroxide solution show high reaction velocity in the 2nd stage dehydration due to

†To whom correspondence should be addressed.
E-mail: scnam@kier.re.kr

the characteristics of the supercritical water, resulting in crystallization. The reaction conditions for the seed products seem to control the final product. In the continuous synthesis of barium hexaferrite using the supercritical water crystallization method, we observe the relationship between changes in temperature, pressure and residence time at each mixing-point and the characteristics of the product.

EXPERIMENTAL

1. Materials and Analysis

In order to facilitate the feeding of materials into the system by the non-pulsation high-pressure pump, $Ba(NO_3)_2$ (Junsei, 98.5%) and $Fe(NO_3)_3 \cdot 9H_2O$ (Showa, 98%), which are highly water soluble and are relatively non-corroding, were dissolved in de-ionized water without additional processing. KOH aqueous solution was also used as a high ionization degree reagent to control the concentration of the anions in the solution. In the aqueous solution, the concentration of $Fe(NO_3)_3 \cdot 9H_2O$ was 0.02 mol and the concentration of $Ba(NO_3)_2$ and of KOH was, respectively, 0.01 mol and 0.32 mol.

The products from the experiment were rinsed with distilled water and dried for 24 hours in a dry oven (60 °C). The crystal structure of the products was analyzed by X-ray diffractometry (XRD, Model D/MAX, Rigaku, CuKα graphite monochromator) at a scan rate of 2° 2θ/min and also by scanning electron micrography (SEM, Model XL-30, Philips). Photographs were analyzed for the shapes and sizes of the particles. Vibrating sample magnetometer (VSM, Model 7300, Lake Shore) was used to measure the magnetic properties (coercivity and saturation magnetization) of the products. During measurement, the maximum applied magnetic field was 10 kOe.

2. Apparatus and Procedure

A diagram of the barium hexaferrite continuous synthesis apparatus is shown in Fig. 1. Barium/iron(III) nitrate mixed solution and KOH aqueous solution were quantitatively fed into the reactor by a high-pressure pump (GL Science Co., Model PUS-11) at a flow rate of 2-4 ml/min. Before injecting into the preheating-zone (MP2), they were mixed at mixing point MP1 at room temperature and under the set pressures. The solution feed rate into the reactor varied depending on the temperatures and/or pressures. The system pressure was controlled by using a back-pressure regulator (Tescom, Model 26-1722-24). The feed solution was combined with the preheated water at 350-450 °C at mixing point MP2. The feed rate was 4-8 ml/min. At the time, the temperature was adjusted to 100-250 °C, the range where the nuclei are formed. For the maintenance of supercritical conditions, the solutions containing the nuclei were mixed with the preheated water at 500-600 °C at mixing point MP3. The external heater was used for minimizing the temperature gradient in the reactor during the reaction. The vertical tubular reactor was made up of 316 stainless steel (length 600 cm, ID 0.32 cm, volume 48.2 cm^3), and the temperature was controlled with a K-type thermocouple and a proportional integral differential (PID) temperature controller, with the temperature distribution being within ±1 °C. The residence time of the solution in the reactor (τ) was evaluated via Eq. (3).

$$\tau = V\rho/F \tag{3}$$

Where V is the reactor volume and F is the mass flow rate, ρ is the density of the feed solution. The residence time at the mixing points and in the reactors was defined as shown in Fig. 2, where τ_1 and τ_2 are the residence time at the mixing points MP2 and MP3, and in the tubular reactor, respectively. The residence time was changed by changing the feed flow in all experiments. The products after the reaction were rapidly cooled by using a heat exchanger in order that residence time could be accurately determined. The fine particles were collected through the in-line filter (Swagelok, Model SS-8F-K4-05, 0.5 μm) and the filtered solution then passed through a back-pressure regulator and was finally collected in a storage tank.

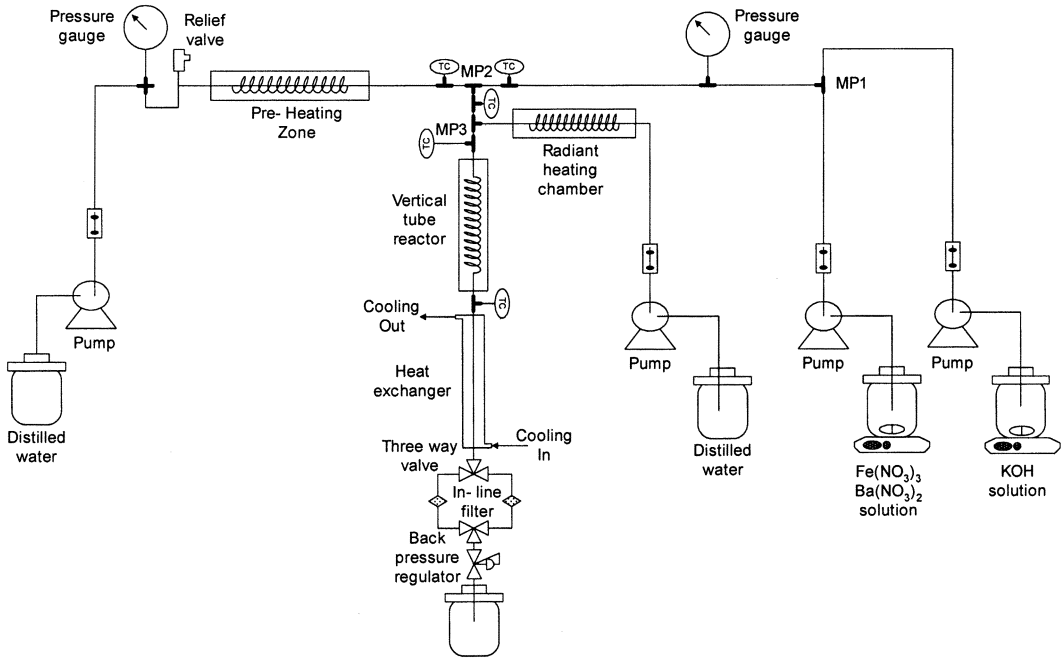


Fig. 1. Schematic diagram of the continuous synthesis apparatus by the supercritical water crystallization method: MP (mixing point).

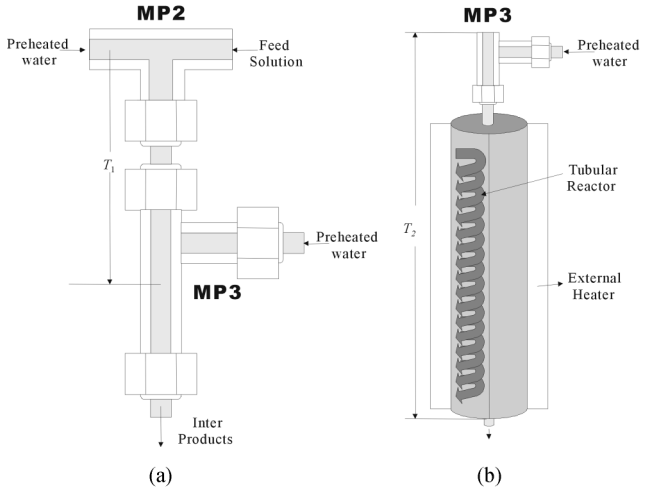


Fig. 2. The definition of the residence time.
(a) τ_1 : the residence time at mixing point MP2
(b) τ_2 : the residence time at MP3 and vertical tubular flow reactor

RESULTS AND DISCUSSION

In this study, as shown in Figs. 1 and 2, the effect of the intermediate phase, which was formed in the 1st stage hydrolysis at MP2 in Fig. 2(a) where the feed solution is mixed with preheated water, on the morphology and structure of the final products in the 2nd stage dehydration by the supercritical water at MP3 was determined.

The experiments include: i) observation of change in the composition and morphology of the hydrolytic products in the 1st stage at MP2 when the temperatures, pressures and residence times were changed; ii) evaluation of the proper critical nuclei formation conditions at MP2 by observing the changes in structure, morphology and magnetic characteristics of the 2nd stage products (formed when the 1st stage products from MP2 were fed to MP3 and to the tubular reactor) with changes in temperature, pressure and residence time in the supercritical condition; and iii) evaluation of the reaction mechanism of the 2nd stage final products by changing the temperature, pressure and residence time at MP3 and the tubular reactor.

1. Characteristics of Particles Formed at MP2

In the continuous synthesis process, mixtures of barium nitrate and ferric nitrate solutions and KOH aqueous solution that were completely dissolved at room temperature are mixed at MP1 before injecting into the preheating-zone (MP2). The hydrolysis between $[NO_3^-]$ and $[OH^-]$ starts at this stage. The mixed aqueous solution is directly fed into MP2 through the supply line.

Hakuda et al. [1998] obtained fine barium hexaferrite in the continuous hydrothermal synthesis apparatus when the Fe/Ba molar ratio of non-stoichiometric and alkali mole ratio of $[OH^-]/[NO_3^-]$ was 2 and 4, respectively. This result shows that excessive $[Ba^{2+}]$ ions suppress the crystal growth, and reduce size of the particles, as the Fe/Ba molar ratio gets lower. When the Fe/Ba molar ratio is lower than 2, the crystallinity decreases rapidly, denoting that the Fe/Ba molar ratio of 2 is appropriate. When the alkali mole ratio is high, the particles size gets smaller. However, fine particles with the size of 0.1 μm or smaller are not produced even if the alkali mole ratio is increased to 4 or higher. Also, other crystal structures are formed when the alkali mole ratio is high. So, it was found that the alkali mole ratio of 4 is most appropriate. Based on above knowledge, the Fe/Ba molar ratio was set at 2 and the alkali mole ratio at 4 in our experiments. We attempted to observe the role of MP2 by watching the change in the characteristics of the particles depending on the change in the temperatures, pressures and residence times at MP2. At MP2, the reaction time (τ_1) was set to 6 s and 40 MPa, and the temperature was varied from 100 to 250 °C. The resulting composition and morphology of the particles were analyzed by XRD and SEM. As shown in the Fig. 3, the unstable amorphous phases tended to convert to crystals as the temperature increased. The structure of the particles was not accurately determined. The SEM pho-

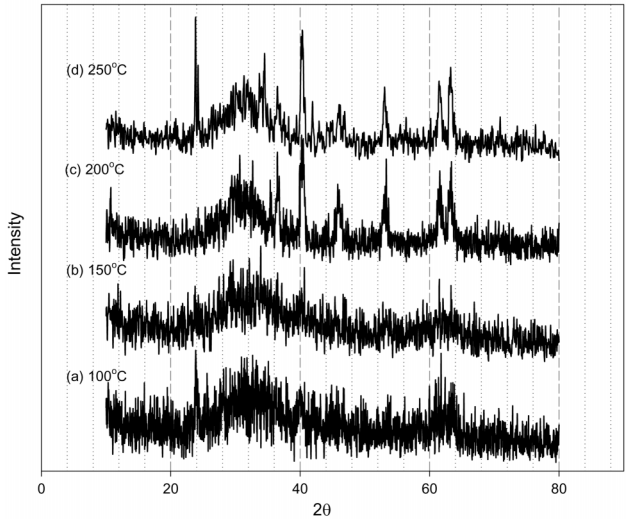


Fig. 3. XRD patterns of the powders obtained with various temperatures of Fig. 2(a) for 6 s at 40 MPa.

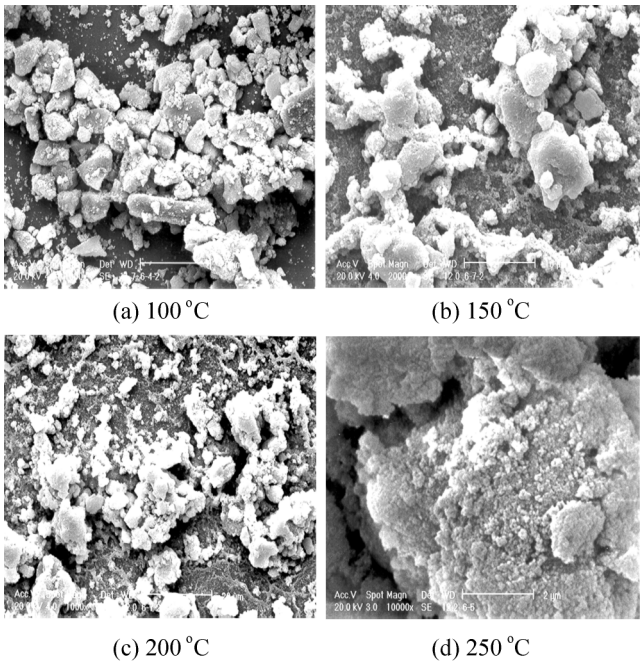


Fig. 4. SEM micrograph of the powders obtained with various temperatures of Fig. 2(a) for 6 s at 40 MPa.

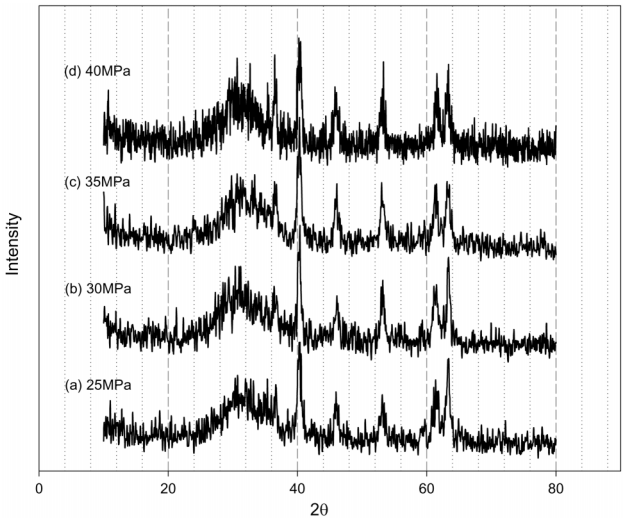


Fig. 5. XRD patterns of the powders obtained with various pressures of Fig. 2(a) for 6 s at 200 °C.

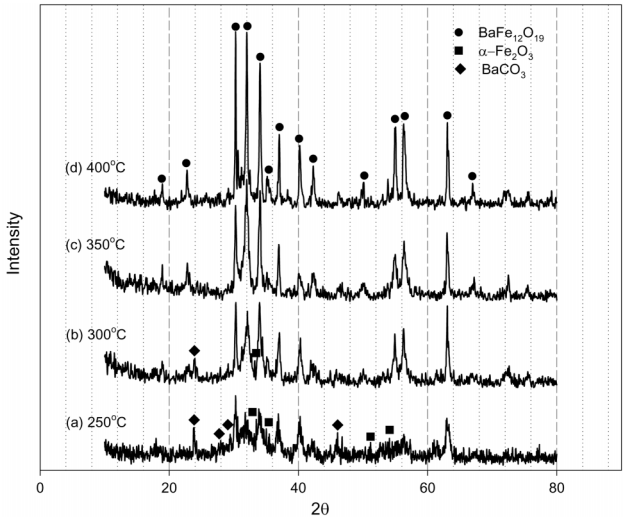


Fig. 6. XRD patterns of the powders obtained with various temperatures of Fig. 2(a) for 20 s at 40 MPa.

tographs in Fig. 4 show the process of agglomeration of the unstable particles as the temperature increased. Likewise, the morphology and composition of the particles were analyzed after variation of the pressures to 25, 30, 35 and 40 MPa, with the same concentration and at the temperature condition of 200 °C. As shown in the XRD pattern in Fig. 5, an amorphous one was formed and change was hardly detected as the pressure increased and agglomeration of the amorphous phases similar to that in Fig. 4 was observed.

The results indicate that, when compared with the hydrothermal synthesis method used by Kumazawa et al. [1993] with ferric nitrate as the precursor, the use of goethite, an intermediate phase, as the starting material reduced the reaction time and the particle size was smaller. In this study, an XRD pattern, which is identical to the particle pattern when goethite was used as the precursor, was obtained. As it is unlikely that the matter is crystallized through dissolution and recrystallization due to the short reaction times, it is thought that the matter exists in the feed solution in the form of unstable amorphous nuclei and then is agglomerated rapidly during cooling. $Fe(NO_3)_3$ aqueous solution was converted into the unstable amorphous $Fe(OH)_3$ or α-FeOOH as the temperature and pressure increased in the alkali condition. This agglomeration velocity is faster than the formation and crystallization velocity for the nuclei and the fine nuclear products should agglomerate immediately after the growth of barium hexaferrite of minimum size. The reaction environment should be controlled so that the degree of agglomeration does not become too high, resulting into larger size of the particles. In conclusion, as shown in the XRD patterns in Fig. 3 and 5, the crystallinity of the products or growth of the nuclei in connection with the 1st stage products at MP2 are predominantly influenced by temperature rather than pressure.

Fig. 6 is the XRD patterns of the formed particle as the residence time (τ_1) and the reaction temperature at MP2 increase. The pressure was fixed at 40 MPa and the temperature at MP2 was changed to 250, 300, 350 and 400 °C and the residence time (τ_1) was increased to 20 s. When the temperature of MP2 was 250 °C, hematite and barium hexaferrite peaks, which did not appear when the residence time was 6 s, as well as unstable non-crystal materials, were produced, showing that the 2nd stage reaction (dehydration) took place. This shows that the intermediate phase may differ depending on the change in the residence times even under the same synthesis conditions. At 300 °C, a small quantity of hematite and barium hexaferrite peak was obtained without the peak of unstable amorphous phase. At 350 °C and higher, the dehydration by high-temperature preheated water was perfectly done and only single-phase barium hexaferrite was formed. As a result of the SEM photographs in Fig. 7, the unstable hematite formed from $Fe(NO_3)_3$ aqueous solution in the supercritical crystallization method was minimum and its morphology could hardly be figured out. The formed barium hexaferrite

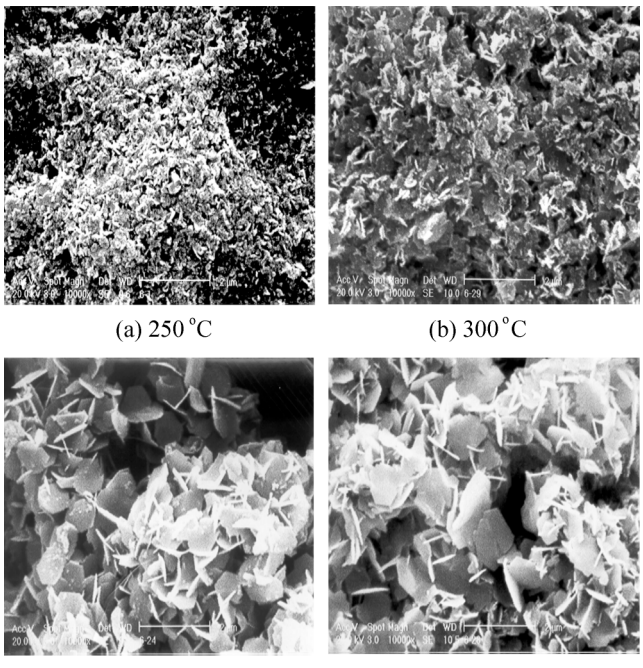


Fig. 7. SEM photographs of the powders obtained with various temperatures of Fig. 2(a) for 20 s at 40 MPa.

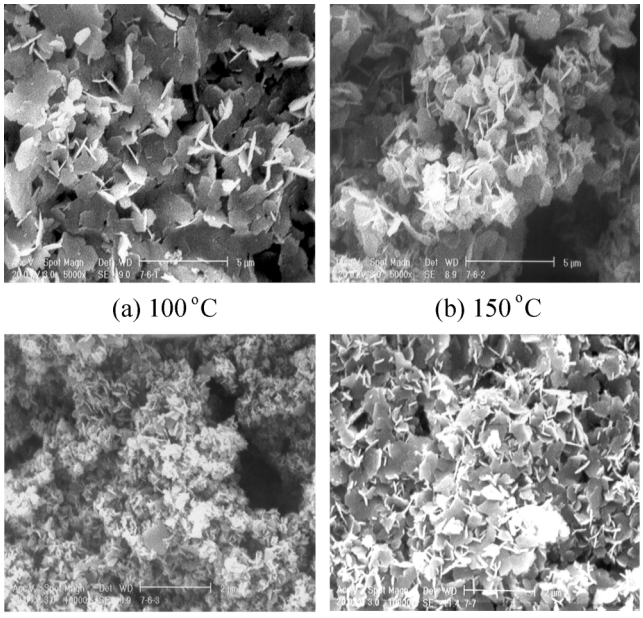
also did not have good crystallinity. The structure of barium hexaferrite formed at 350 °C or higher was of thin hexagonal plane and its particle size on the average was 1 μm. The crystallinity and distribution of particles were both unsatisfactory.

The result shows that, while barium hexaferrite formation is possible at MP2 with only the preheated water that is supplied for the hydrolysis at the 1st stage and for the preheating of the metal salt aqueous solution, the rapid temperature increase with the injection of preheated water at 500-600 °C causes the instability in the whole system and rapid increase of supersaturation and they in turn deteriorate the crystallinity of the products. Generally, large particle sizes may result during the conversion of hematite to barium hexaferrite due to crystal growth by Ostwald ripening [Wang et al., 1994]. Therefore, the temperature, pressure and residence time at MP2, where seed products are formed for the production of fine particles are very influential on the production of fine barium hexaferrite. Too rapid temperature increase will cause adverse effects including the reduction of the distribution of the particles produced and generation of byproducts such as hematite. It is determined that 200 °C, 40 MPa, 6 s are appropriate conditions for the reaction.

2. Characteristics of Particles Produced at MP3 and Vertical Tubular Flow Reactor

In the synthesis of metal oxides, the effect of the feed solution on the initial density is very limited, while the reaction temperature and pressure has a pronounced effect on the particle sizes than other parameters [Adschiri et al., 1992]. Based on the above result of the experiment on the influence of MP2, the 1st stage hydrolytic products were treated for residence time (τ_2) from 40 to 100 seconds at MP3 and in the tubular reactor at temperatures of 300, 350, 400 and 450 °C and at pressures of 30, 35 and 40 MPa and the resulting dehydrated products were studied for changes in crystal structure and morphology.

When the pressure was fixed at 40 MPa, the hydrolytic products formed at MP2 were converted into single-phase barium hexaferrite through the dehydration and re-crystallization procedures at MP3 depending on the temperature change. Looking at the SEM photographs in Fig. 8, however, at the temperatures of 100 and 150 °C, where the unstable non-crystal materials were formed at MP2 as shown in Fig. 3, unstable barium hexaferrite with a particle size of 2 μm was obtained, while at 200 °C stable barium hexaferrite with fine and even particle sizes of 0.1-0.2 μm was formed. At 250 °C



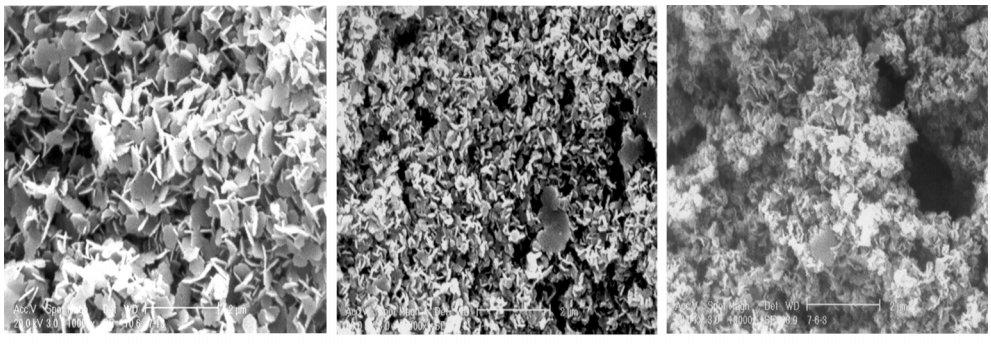
(a) 100 °C (b) 150 °C

(c) 350 °C (d) 250 °C

Fig. 8. SEM photographs of the powders obtained at Fig. 2(b) with various temperatures of Fig. 2(a) (40 MPa, MP3=400 °C, τ_1=6 s, τ_2=80 s).

at MP2, the particle size was a bit bigger than that of the particles obtained at 200 °C, because the nuclei that were bigger than the amorphous phase produced at 200 °C were formed into particles through the dehydration and recrystallization. The magnetic properties of saturation magnetization and coercivity were enhanced by increasing the residence time. The saturation magnetization jumped up to about 65 emu/g when sample reaction time increased from 80 s to 100 s [Nam et al., 2001]. Next, MP2 and 3 were fixed at 200 °C and 400 °C, respectively, and then sizes and morphologies of particles were observed at 30, 35 and 40 MPa. According to Fig. 9, no change was made in the structure of particles by the increase or decrease of pressure, while the size of barium hexaferrite decreased as the pressure increased.

The results apparently show that, by the physical and chemical properties of the supercritical water, the increase in pressure increased the concentration of [$BaOH^+$] by the dissolution equilibrium the



(a) 30 MPa (b) 35 MPa (c) 40 MPa

Fig. 9. SEM photographs of the powders obtained at Fig. 2(b) with various pressures in the continuous process (MP2=200 °C, MP3=400 °C, τ_1=6 s, τ_2=80 s).

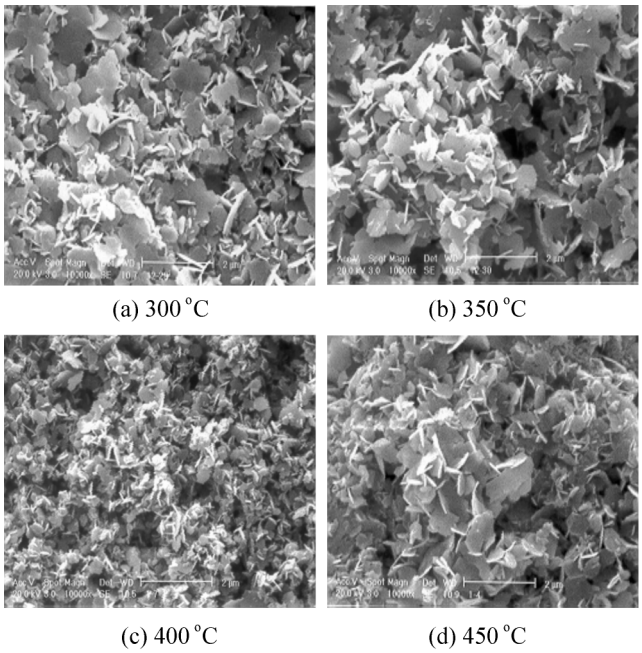


Fig. 10. SEM photographs of the powders obtained with various temperatures of Fig. 2(b) (40 MPa, MP2=200 °C, τ_1=6 s, τ_2=80 s).

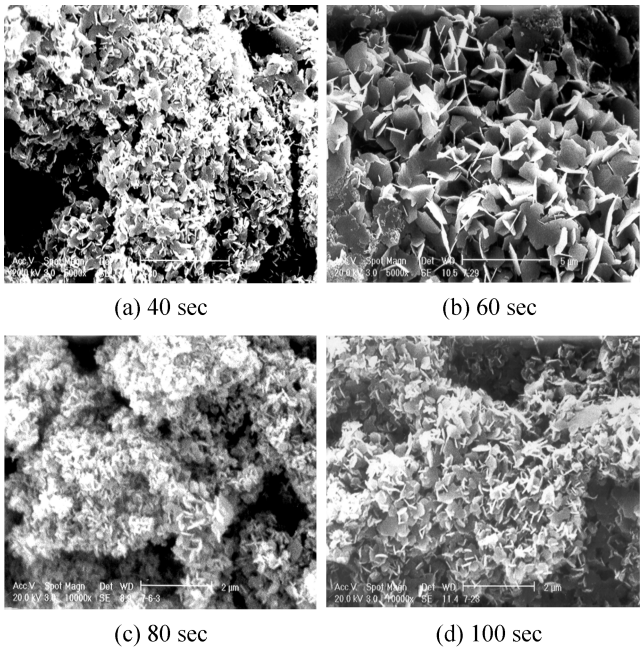


Fig. 11. SEM photographs of the powders obtained with various residence time (τ_2) of Fig. 2(b) (40 MPa, MP2=200 °C, MP3 =400 °C, τ_1=6 s).

reaction $[Ba^{2+}]+[OH^-]\leftrightarrow[BaOH^+]$. In other words, the quantity of nuclei increased and the formation of barium hexaferrite was facilitated by the unstable $Fe(OH)_3$ affecting $[BaOH^+]$ through the penetration- and diffusion-based dehydration. This allows for the formation of barium hexaferrite with fine and good size distribution. Therefore, the crystallinity of the 1st stage hydrolytic products synthesized at MP2 and the proper critical nuclei formation conditions have a strong effect on the shapes and sizes of the particles of the 2nd stage final products.

XRD pattern showed that single-phase barium hexaferrite was obtained throughout all ranges as the temperature at MP3 was increased from 300 °C to 450 °C. According to the SEM photograph in Fig. 10, the size of the particles formed at 400 °C was 0.1-0.2 μm and the morphologies were also excellent. At 450 °C, however, the distribution of particle was widened presumably due to the dissolution and recrystallization of fine particles with a size of 0.1-0.2 μm, which were rapidly produced by the temperature increase.

Fig. 11 shows SEM photographs of particles obtained at various residence times at MP3 and in the tubular flow reactor. Throughout the range, single-phase barium hexaferrite was found. Particles with a low degree of crystallinity are obtained at residence times of 40 sec and 60 sec. The crystallinity of these particles was unsatisfactory. The residence time has to be very short to obtain good crystallinity. However, barium hexaferrite of size 0.1-0.2 μm was obtained at residence times over 80s. At the residence time of 80 s or higher, the size reduction effect was small, because of the dissolution and recrystallization of the formed barium hexaferrite which caused a widened distribution of particles and an increase in particle size.

Therefore, the study found the optimum conditions at MP2: 200 °C, 40 MPa and 6 s. The optimum conditions at MP3 and in the tubular flow reactor were: 400 °C, 40 MPa and 80 s. Under the conditions, single-phase barium hexaferrite with a size of 0.1-0.2 μm were obtained as the 2nd stage final products.

CONCLUSIONS

It was confirmed that in the supercritical water crystallization process, $BaO\cdot6Fe_2O_3$ synthesis follows the nonstoichiometric reaction path. In the $BaFe_{12}O_{19}$ formation reaction, the reaction kinetics is 10 times faster than the batch type hydrothermal synthesis method. Single-phase $BaO\cdot6Fe_2O_3$ could also be synthesized in the continuous synthesis process using the supercritical water crystallization method.

The details of the derived conclusions are as follows:

1. For the production of fine particles formed through the hydrolysis, the temperature should be maintained at 200 °C. The effect of the pressure was not significant. Also, since α-Fe_2O_3 and barium hexaferrite are produced together with increasing the residence time, the residence time should be less than 10 s;

2. The final product produced through the dehydration based on the change in temperatures, pressures and residence times, generally reduces the particle sizes as the reaction temperature is increased. However, the reduction effect was low at temperature of 400 °C or higher. Increasing the reaction pressure also reduced the particle size. On the other hand, increasing the residence time decreased the particle size, while the residence time of 80 s or longer did not reduce the size of the particles; and

3. The operating conditions are 200 °C, 40 MPa and 6 s and the critical nuclei are formed through the hydrolysis for the production of fine particles in tubular flow reactor (MP3) and 400 °C, 40 MPa and residence time of 80 s in tubular flow reactor where the dehydration takes place. Under the conditions, single-phase barium hexaferrite with a size of 0.1-0.2 μm was obtained as the final products.

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