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Preparation of barium iron oxides by the oxidation of iron in the Fe–Ba(OH)$_2$–NaOH–H$_2$O–O$_2$ system

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Iron was oxidized in the Fe–Ba(OH)$_2$–NaOH–H$_2$O–O$_2$ system at elevated temperatures. Fe_3O_4 and α-FeOOH were formed in the absence of oxygen. On the other hand, hexagonal plate-like particles of $BaFe_{12}O_{19}$, 1.0–4.3 μm diameter, were formed as single phase by the oxidation of iron in Ba(OH)$_2$ and NaOH mixed solutions at 250–300 °C and above 1.0 MPa oxygen. The diameter of the particle significantly depended on the NaOH concentration. Additives such as CO_3^{2-}, SO_4^{2-} and CH_3COO^- promoted the grain growth of $BaFe_{12}O_{19}$.

1. Introduction

The preparation of ceramic materials by the hydrothermal oxidation of metals and metal alloys has received attention because of advantages such as high purity, excellent morphology of the product, high reaction rate, lack of alkali and acid consumption for neutralization, etc. In previous work [1–4], it was reported that various iron oxides, such as α-Fe_2O_3, Fe_3O_4, α-$NaFeO_2$, γ-Fe_2O_3, $Li_xFe_{3-x}O_4$ and α-$LiFeO_2$ could be formed by the hydrothermal oxidation of iron in alkaline solutions such as sodium hydroxide, potassium hydroxide and lithium hydroxide solutions. The chemical composition and morphology of the product significantly changed depending on the kind and concentration of alkaline solution and coexisting salt, partial pressure of oxygen, temperature, etc. In the present work, the oxidation behaviour of iron in the Fe–Ba(OH)$_2$–NaOH–H$_2$O–O$_2$ system was investigated.

2. Experimental procedure

The reagent-grade reduced iron powder of mean particle size of about 100 μm, was used as starting material. NaOH and Ba(OH)$_2$ were of reagent grade and used without further purification. Hydrothermal oxidation of iron powders in the presence of pressurized oxygen was conducted in an SUS 316 type stainless steel autoclave of 300 cm^3 internal volume, equipped with polytetrafluoroethylene (Teflon) cup inserts of 2 mm wall thickness and a magnet driving stirrer. The stirring rod and blade were coated with Teflon tape to avoid corrosion.

A typical experiment proceeded as follows: 3 g reduced iron powder, 50 g water and 10–150 g NaOH and Ba(OH)$_2$ were placed into a Teflon cup contained in an autoclave, and then the autoclave was sealed. After purging the air with nitrogen, the autoclave was placed in an electric furnace, and then the temperature was raised at about 6 °C min^{-1} to the desired temperature under saturated vapour pressure; oxygen gas was then injected into the autoclave up to 3 MPa, to initiate the oxidation reaction. During the reaction period, the suspensions were agitated at the rate of 1200 r.p.m. and the oxygen partial pressure was kept at 3 MPa. After holding at the desired temperature for 2 h, the autoclave was removed from the electric furnace, and cooled quickly in air.

The oxidation of iron powder in the absence of oxygen was conducted in a 20 cm^3 sealed stainless steel reactor equipped with Teflon cup inserts of 1 mm wall thickness as follows. After placing 0.2 g iron powder, 3 g distilled water and desired amounts of Ba(OH)$_2$ into the tube reactor, the tube was placed in a silicone oil bath, set at the desired temperature, and held in it for the desired time, then cooled quickly with water.

The reaction products were taken out and separated centrifugally, rinsed with 10 vol% acetic acid solution and water in order to avoid contamination with barium carbonate, and dried at 105 °C for 12 h. The crystalline phases of the products were determined by X-ray powder diffraction analysis (XRD) using iron filtered CoK_α radiation.

3. Results and discussion

The phase composition of the precipitates obtained by the hydrothermal oxidation of iron powders in 2–6.63 M Ba(OH)$_2$ solutions at 100–250 °C in the absence of oxygen for 2 h, is shown in Fig. 1. In a previous paper [4] it was reported that the hydrothermal oxidation of the same iron powder in NaOH, KOH and LiOH solutions proceeded above 150 °C, but in Ba(OH)$_2$ solution it began at a significantly lower temperature, such as 100 °C, although iron was not oxidized completely even at 250 °C. These results indicated that the hydrothermal oxidation of iron in Ba(OH)$_2$ proceeded more rapidly than those in NaOH, KOH and LiOH solutions in the initial stage

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of reaction, but thereafter the reaction was depressed due to the formation of a protective oxide film on the surface of iron. The reaction products in $Ba(OH)_2$ solutions were Fe_3O_4 at lower temperature, but α-FeOOH at higher temperature. The increase in $Ba(OH)_2$ concentration greatly decreased the critical temperature above which α-FeOOH was formed, but no formation of barium ferrite was observed under the present reaction conditions.

The phase composition of the precipitates obtained by the oxidation of iron powders in mixed solutions consisting of 0.2 M $Ba(OH)_2$ and 1–10 M NaOH at 200–300 °C and 3 MPa oxygen for 2 h is shown in Fig. 2. In the presence of NaOH and oxygen, the oxidation of iron was greatly promoted, i.e. iron was completely oxidized in the presence of more than 3 M NaOH above 250 °C. The oxidation products were γ-Fe_2O_3 at lower temperature and $BaFe_{12}O_{19}$ at higher temperature. $BaFe_4O_7$ was also formed in 0.2 M $Ba(OH)_2$–3 M NaOH mixed solution at 250 °C. The critical temperature below which γ-Fe_2O_3 formed increased with increasing NaOH concentration, whereas that above which $BaFe_{12}O_{19}$ formed, was decreased. Consequently, $BaFe_{12}O_{19}$, which has received attention for application as permanent magnets [5], was formed as single phase in 0.2 M $Ba(OH)_2$ and 3–6 M NaOH mixed solutions at 275 °C and 0.2 M $Ba(OH)_2$ and 1–7 M NaOH mixed solutions at 300 °C. The formation of barium ferrite such as $BaFe_{12}O_{19}$, $BaFe_9O_{14.5}$ and $BaFe_4O_7$ by the hydrothermal reactions of $Fe(NO_3)_3$–$Ba(NO_3)_2$–NaOH, α-FeOOH–$Ba(OH)_2$, β-FeOOH–$Ba(OH)_2$, γ-FeOOH–$Ba(OH)_2$ and α-Fe_2O_3–$Ba(OH)_2$ has been reported by Kiyama [6], but this is the first report of the formation of barium ferrite by the oxidation of iron under hydrothemal conditions.

A scanning electron micrograph and powder X-ray diffraction pattern of the precipitates formed by the oxidation of iron powder in 0.2 M $Ba(OH)_2$ and 5 M NaOH mixed solution at 300 °C and 3 MPa oxygen for 2 h, are shown in Figs 3 and 4, respectively. Hexagonal platelets, 1.6 µm average diameter, were observed. The molar ratio of Fe/Ba in the product was 12, indicating that the product was stoichiometric $BaFe_{12}O_{19}$. All X-ray diffraction peaks could be indexed as $BaFe_{12}O_{19}$, although the peak intensity ratio was different from that of the JCPDS card [7]. The major difference was in the 006 and 008 lattice planes, where the peak intensities of these planes were significantly stronger than that shown in the card, indicating the plane of hexagonal platelets was $\{001\}$.

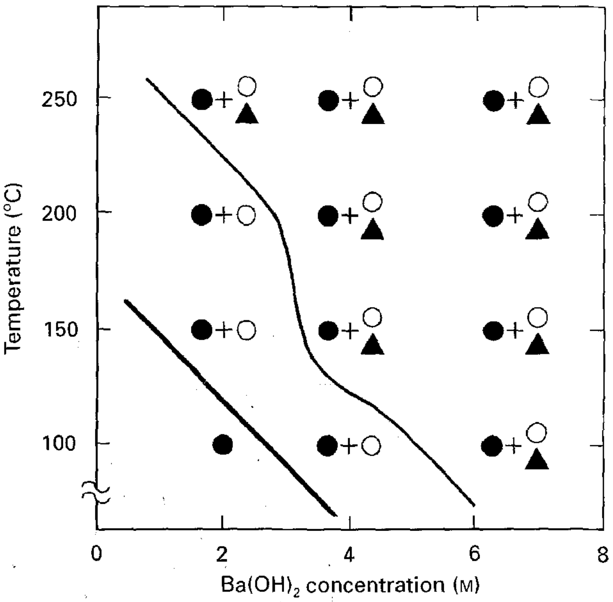

Figure 1 Phase composition of the precipitates obtained by the hydrothermal oxidation of iron powders in various concentrations of $Ba(OH)_2$ solutions at various temperatures for 2 h in the absence of oxygen (●) Fe, (○) Fe_3O_4, (▲) α-FeOOH.

Crystalline phases of the precipitates and the average diameter of the $BaFe_{12}O_{19}$ particle obtained by the oxidation of iron powders in the mixed solutions of 5 M NaOH and various concentrations of $Ba(OH)_2$ at 300 °C and 3 MPa oxygen for 2 h, are summarized in Table I. Hexagonal platelets of $BaFe_{12}O_{19}$ ferrite, 1.8 and 1.6 µm diameter, were formed as single phase in the solution containing 0.1 and 0.2 M $Ba(OH)_2$,

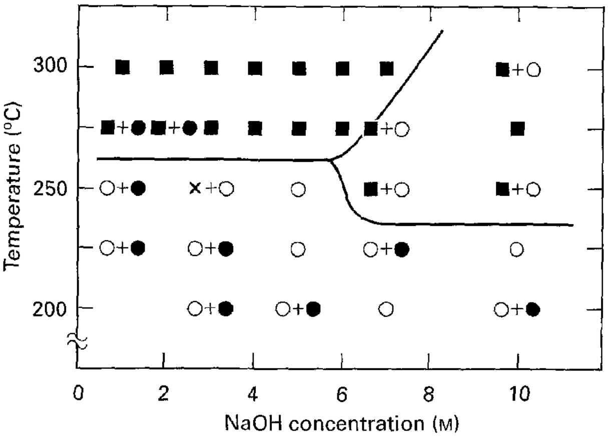

Figure 2 Phase composition of the precipitates obtained by the oxidation of iron powders in the solutions containing 0.2 M $Ba(OH)_2$ and various concentrations of NaOH at various temperatures and 3 MPa oxygen for 2 h. (●) Fe, (○) γ-Fe_2O_3, (x) $BaFe_4O_7$ (■) $BaFe_{12}O_{19}$.

Figure 3 Scanning electron micrograph of the product obtained by the oxidation of iron powders in 0.2 M $Ba(OH)_2$–5 M NaOH mixed solution at 300 °C and 3 MPa oxygen for 2 h.

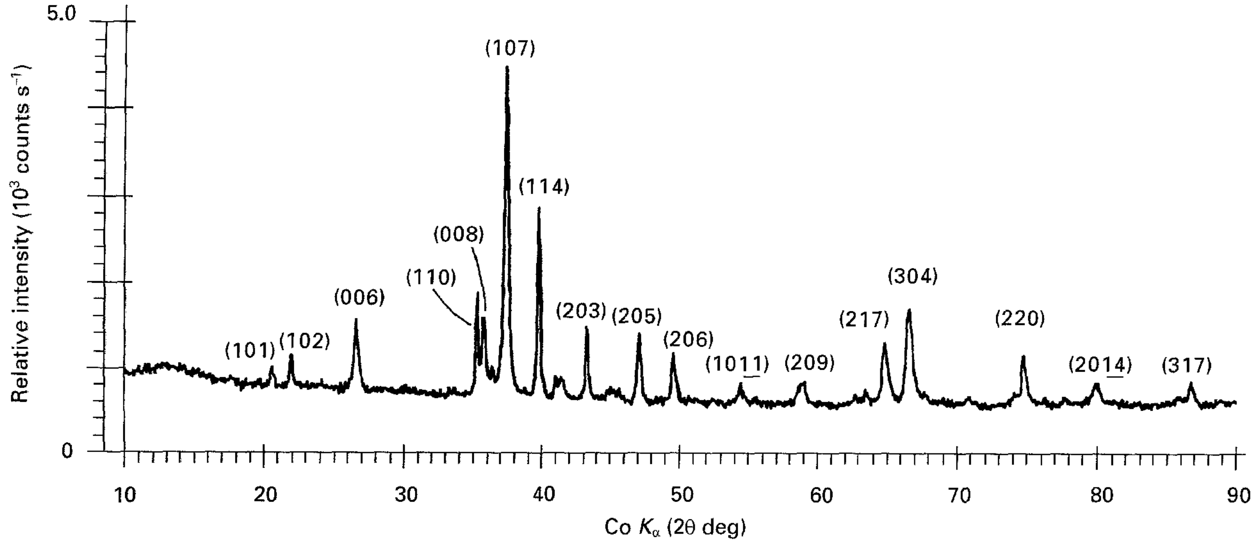

Figure 4 X-ray diffraction pattern of the precipitates formed by the oxidation of iron powders in 0.2 M $Ba(OH)_2$–5 M NaOH mixed solution at 300 °C and 3 MPa oxygen for 2 h.

TABLE I Phase composition of the precipitates and the average diameter of $BaFe_{12}O_{19}$ platelets obtained by the oxidation of iron powders in mixed solutions of 5 M NaOH and various concentrations of $Ba(OH)_2$ at 300 °C and 3 MPa oxygen for 2 h

Concentration of $Ba(OH)_2$ (M)	Phase composition	Average diameter of $BaFe_{12}O_{19}$ (μm)
0.07	$BaFe_{12}O_{19}$ + Fe_3O_4	
0.1	$BaFe_{12}O_{19}$	1.8
0.2	$BaFe_{12}O_{19}$	1.6
0.4	γ-Fe_2O_3	
0.6	γ-Fe_2O_3	
0.8	γ-Fe_2O_3	

TABLE II Phase composition of the precipitates and the average diameter of $BaFe_{12}O_{19}$ platelets obtained by the oxidation of iron powders in 0.2 M $Ba(OH)_2$–5 M NaOH mixed solutions at 300 °C and various oxygen pressure for 2 h

Oxygen pressure (MPa)	Phase composition	Average diameter of $BaFe_{12}O_{19}$ (μm)
0	Fe_3O_4	–
0.5	Fe_3O_4	–
1.0	$BaFe_{12}O_{19}$	1.5
2.0	$BaFe_{12}O_{19}$	1.4
3.0	$BaFe_{12}O_{19}$	1.6

respectively. Fe_3O_4 was formed together with $BaFe_{12}O_{19}$ in the solution containing 0.07 M $Ba(OH)_2$. This might be due to the shortage of Ba^{2+} in the solution, because the Ba/Fe molar ratio in the 0.07 M $Ba(OH)_2$ solution was 0.78 of the stoichiometric value for $BaFe_{12}O_{19}$. On the other hand, γ–Fe_2O_3 was formed above 0.4 M $Ba(OH)_2$. These results suggest that excess $Ba(OH)_2$ depressed the formation of $BaFe_{12}O_{19}$ and promoted the formation of γ–Fe_2O_3. Depression of $BaFe_{12}O_{19}$ formation by excess $Ba(OH)_2$ was also reported for the hydrothermal reactions of α–FeOOH and $Ba(OH)_2$ at 200–300 °C [6].

Crystalline phases of the precipitates and the average diameter of $BaFe_{12}O_{19}$ particles obtained by the oxidation of iron powders in 0.2 M $Ba(OH)_2$ and 5 M NaOH mixed solutions at 300 °C and 0–3.0 MPa oxygen for 2 h, are listed in Table II. The oxidation products were Fe_3O_4 below 0.5 MPa oxygen and hexagonal platelets of $BaFe_{12}O_{19}$, 1.4–1.6 μm diameter, above 1.0 MPa, respectively, indicating that oxygen is essential to form $BaFe_{12}O_{19}$ but the grain size of $BaFe_{12}O_{19}$ does not depend significantly on the oxygen pressure.

The diameter of $BaFe_{12}O_{19}$ formed by the oxidation of iron powder in mixed solutions of 0.2 M $Ba(OH)_2$ and 1–6 M NaOH at 300 °C and 5 MPa oxygen for 2 h is shown in Fig. 5 as a function of NaOH concentration. The diameter increased from 1.3 μm to 1.9 μm with increasing NaOH concentration from 1 M–4 M, and thereafter decreased to ~1.6–1.7 μm in 5–6 M NaOH solutions. The increase in NaOH concentration may have resulted in increasing solubility of FeO_2^-, but a decreasing solubility of Ba^{2+}. The two opposing effects might give rise to a maximum crystal growth rate of $BaFe_{12}O_{19}$.

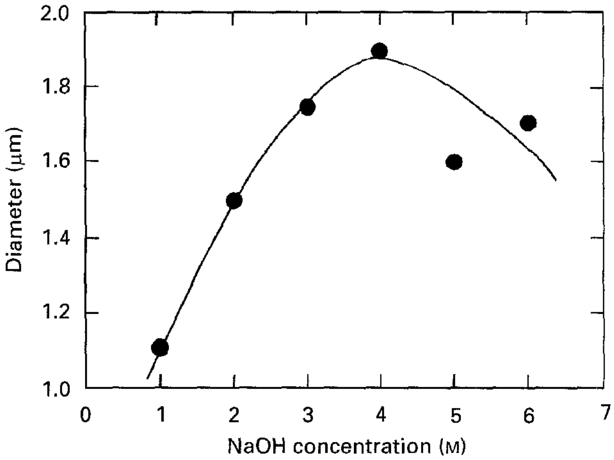

Figure 5 Average diameter of $BaFe_{12}O_{19}$ platelets formed by the oxidation of iron powders in mixed solutions of 0.2 M $Ba(OH)_2$ and various concentrations of sodium hydroxide at 300 °C and 5 MPa oxygen for 2 h.

The time dependence of the diameter of hexagonal platelets of $BaFe_{12}O_{19}$ formed by the oxidation of iron powder in 0.2 M $Ba(OH)_2$ and 5 M NaOH mixed solutions at 300 °C and 3 MPa oxygen, is shown in Fig. 6. The diameter increased linearly with time. Because no formation of new nuclei and/or necks in the particle was observed, a dissolution–reprecipitation mechanism was most likely as the grain–growth mechanism.

The effect of coexisting anions on the phase composition of the products and the diameter of $BaFe_{12}O_{19}$ formed by the oxidation of iron powder in 0.2 M $Ba(OH)_2$ and 5 M NaOH mixed solutions at 300 °C and 3 MPa oxygen for 2 h, is summarized in Table III. The addition of Cl^- and NO_3^- produced no noticeable effect on the phase composition and grain size, whereas the diameter of $BaFe_{12}O_{19}$ platelets increased with increasing CH_3COO^- concentration. The increase in the diameter on the addition of CH_3COO^- might be due to the selective adsorption of CH_3COO^- on the (0 0 1) plane of $BaFe_{12}O_{19}$. On the other hand, the addition of 0.04 M CO_3^{2-} and SO_4^{2-} greatly increased the diameter of $BaFe_{12}O_{19}$ platelets, but the addition of 0.24 M CO_3^{2-} and SO_4^{2-} resulted not in the formation of $BaFe_{12}O_{19}$, but α-Fe_2O_3. The increase in the diameter on the addition of small amounts of CO_3^{2-} and SO_4^{2-} might be due to the decrease in the number of nuclei of $BaFe_{12}O_{19}$ formed by the decreasing soluble Ba^{2+} concentration, because the solubilities of $BaCO_3$ and $BaSO_4$ are small. On the other hand, the formation of α-Fe_2O_3 by the addition of excess CO_3^{2-} and SO_4^{2-} might be due to the complete precipitation of Ba^{2+} as $BaCO_3$ and $BaSO_4$.

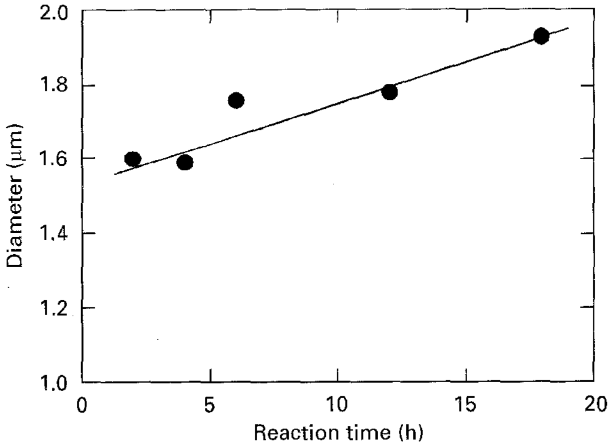

Figure 6 Time dependence of the average diameter of $BaFe_{12}O_{19}$ platelets formed by the oxidation of iron powder in 0.2 M $Ba(OH)_2$–5 M NaOH mixed solutions at 300 °C and 3 MPa oxygen for 2 h.

TABLE III Effect of coexisting anions on the diameter of $BaFe_{12}O_{19}$ platelets and phase composition of the products formed by the oxidation of iron powder in 0.2 M $Ba(OH)_2$–5 M NaOH mixed solutions at 300 °C and 3 MPa oxygen for 2 h

Anion	Concentration (M)	Phase composition	Diameter of $BaFe_{12}O_{19}$ (µm)
None	–	$BaFe_{12}O_{19}$	1.6
CO_3^{2-}	0.2	$BaFe_{12}O_{19}$	4.3
	1.2	α-Fe_2O_3	–
SO_4^{2-}	0.2	$BaFe_{12}O_{19}$	3.1
	1.2	α-Fe_2O_3	–
Cl^-	0.4	$BaFe_{12}O_{19}$	1.6
	1.4	$BaFe_{12}O_{19}$	1.6
NO_3^-	0.4	$BaFe_{12}O_{19}$	1.8
	1.4	$BaFe_{12}O_{19}$ + $BaFe_4O_7$	1.6
CH_3COO^-	0.4	$BaFe_{12}O_{19}$	1.8
	1.4	$BaFe_{12}O_{19}$	2.3
	2.9	$BaFe_{12}O_{19}$	2.5

4. Conclusions

From the present experimental results, the following conclusions may be drawn.

1. Hexagonal plate-like particles of $BaFe_{12}O_{19}$, 1.0–4.3 µm diameter, were formed as single phase by the oxidation of iron in $Ba(OH)_2$ and NaOH mixed solutions at 250–300 °C and above 1.0 MPa oxygen.
2. The diameter of the particle significantly depended on the NaOH concentration, but not on the partial pressure of oxygen.
3. Small amounts of CO_3^{2-} and SO_4^{2-} promoted the grain growth of $BaFe_{12}O_{19}$, whereas excess amounts of those ions depressed the formation of $BaFe_{12}O_{19}$ and promoted the formation of α-Fe_2O_3.
4. The particle size of $BaFe_{12}O_{19}$ increased with increasing concentration of CH_3COO^-.

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