

The Formation of α -Fe₂O₃ and BaFe₁₂O₁₉ in the Presence of Iron (II) Hydroxide and Nitrates with or without Ba (II)

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Alkaline suspensions containing 0.45M FeCl₂ and different concentrations of excess NaOH and of NaNO₃ were subjected to autoclaving between 150 and 250°C. Disklike α -Fe₂O₃ particles were formed with or without the formation of isotropic Fe₃O₄ ones above 180°C. Ferromagnetic platelike BaFe₁₂O₁₉ particles were also formed in the presence of Ba(II) and Fe(II) with the 1:8 atomic ratio under the conditions similar to those for the α -Fe₂O₃ formation. The magnetic properties of the BaFe₁₂O₁₉ sample were investigated at room temperature.

KEY WORDS : Fe(OH)₂ / α -Fe₂O₃ / BaFe₁₂O₁₉ / Ferromagnetic precipitate / Coercivity
/Autoclaving /Alkaline suspension

Introduction

It is known that platelike particles of α -Fe₂O₃ can be formed by autoclaving of alkaline suspension of iron (III) species, such as γ -Fe₂O₃,¹⁾ iron (III) hydroxide²⁾ or α -FeO(OH) at temperatures above 160°C.³⁾ It is also known that a ferromagnetic precipitate of BaFe₁₂O₁₉ can be prepared in the presence of Ba(OH)₂ and either iron (III) hydroxide or α -FeO(OH) with the 1:8 atomic ratio under the conditions where the transformation into α -Fe₂O₃ proceeded.^{4,5)} It was reported that the aging of Fe(OH)₂ suspensions containing nitrates at 90°C gave Fe₃O₄ particles with or without formation of α -FeO(OH) ones, no α -Fe₂O₃ having been obtained.⁶⁾

We have found that the addition of nitrates enables the use of Fe(II) as the source of platelike α -Fe₂O₃ and ferromagnetic BaFe₁₂O₁₉ particles. This paper describes the conditions for the formation of α -Fe₂O₃ by autoclaving Fe(OH)₂ and also for the formation of BaFe₁₂O₁₉ from Fe(II) and Ba(II), both in the presence of nitrates. The magnetic properties of BaFe₁₂O₁₉ at room temperature for the samples in this work are also reported.

Experimental

An acidic solution was prepared in a 1 dm³ autoclave made of stainless steel, by mixing aqueous solutions of NaNO₃ and FeCl₂ (each of reagent grade). To this a NaOH solution was added and each resulting suspension was diluted with conductivity water to 0.7 dm³. A number of alkaline suspensions of Fe(OH)₂, each containing 0.45M (M = mol/dm³) Fe(II), were prepared by varying the concentrations of excess NaOH and nitrates. They were heated to

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the desired temperatures at a rate of $3^{\circ}\text{C min}^{-1}$, kept at 150, 180, 200, 230, or 250°C with mechanical stirring at 550 rpm for a fixed time of 2h and then allowed to cool to room temperature. The resulting products were separated by filtration, well washed with water, and then dried at 80°C in air.

Acidic solutions containing Fe(II) and Ba(II) with the 8:1 atomic ratio were prepared by dissolving BaCl_2 in the acidic solutions mentioned above. Alkaline suspensions were prepared and subjected to autoclaving under the conditions similar to those described above. The ferromagnetic suspensions were treated with 1M HCl until the pH decreased to 2 to remove remaining Ba(II) as a carbonate, which was formed with carbon dioxide from the atmosphere, before the separation by filtration.

The products were subjected to examinations by X-ray diffraction using $\text{FeK}\alpha$ radiation (XRD), scanning electron microscopic observation (SEM), and to the BET surface area measurement using nitrogen. The Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ contents in the products prepared in the absence of Ba(II) were determined by comparing the relative intensities of XRD peaks of Fe_3O_4 d(311) 2.53 and $\alpha\text{-Fe}_2\text{O}_3$ d(104) 2.69Å. Magnetic measurements on the ferromagnetic samples, which had been packed with 1.2–2.0 in packing densities, were carried out at room temperature in a magnetic field up to 10 kOe ($1 \text{ kOe} = 10^6/4 \pi \text{ Am}^{-1}$), by using a vibrating-sample magnetometer.

Results and Discussion

The starting, alkaline suspensions containing 0.45M FeCl_2 , 0.15M NaNO_3 and different amounts of excess NaOH were subjected to autoclaving at temperatures between 150 and 250°C . Fe_3O_4 was formed with $\alpha\text{-FeO(OH)}$ at 150°C , whereas $\alpha\text{-Fe}_2\text{O}_3$ was formed with or without Fe_3O_4 at temperatures above 180°C depending on the concentration of excess NaOH and temperature. The typical iron oxide samples prepared under the various conditions are given in Table 1. The shape of $\alpha\text{-Fe}_2\text{O}_3$ particles formed depended on the concentration of excess NaOH (Fig. 1).

Table 1. Products Obtained by Autoclaving at Different Temperatures, T, Alkaline Suspensions Containing 0.45M Fe(OH)_2 , 0.15M NaNO_3 and Either 0.3 or 6.0M Excess NaOH.

Sample	NaOH/M	T/ $^{\circ}\text{C}$	Contents	
			$\alpha\text{-Fe}_2\text{O}_3$	Fe_3O_4
A*	0.3	180	0	0.83
B	6.0	180	0.19	0.81
C	0.3	200	0.28	0.72
D	6.0	200	1.0	0
E	0.3	230	0.37	0.63
F	0.3	250	1.0	0

* Consisted of $\alpha\text{-FeO(OH)}$ in place of $\alpha\text{-Fe}_2\text{O}_3$

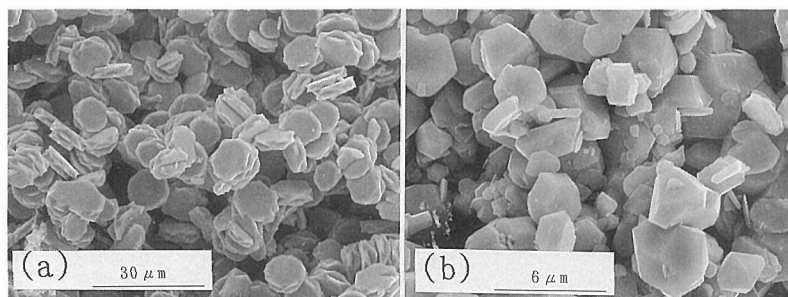


Fig. 1. SEM photographs of the α -Fe₂O₃ samples D(a) and F(b).

In order to investigate the effect of the concentration of the nitrates on the formation of α -Fe₂O₃ under the conditions for the formation of Fe₃O₄ with α -Fe₂O₃, the alkaline suspensions containing 0.9M NaNO₃, 0.45M FeCl₂, and different concentrations of excess NaOH were subjected to autoclaving at temperatures above 180°C. The α -Fe₂O₃ content in the products remarkably increased with increasing the concentrations of NaNO₃ and excess NaOH. In these experiments, the nitrate concentration required for the formation of α -Fe₂O₃ decreased with increases in the temperature and the concentration of excess NaOH. For instance, α -Fe₂O₃ was formed without the formation of Fe₃O₄ at 180°C in the presence of 0.9M NaNO₃ and 6M excess NaOH, and at 250°C in the presence of 0.08M NaNO₃ and 0.3M excess NaOH (Fig. 2).

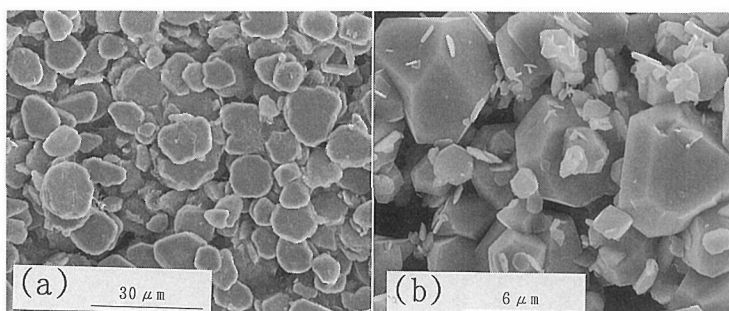


Fig. 2. SEM photographs of the α -Fe₂O₃ samples prepared at 180°C in the presence of 0.9M NaNO₃ and 6M NaOH (a), and at 250°C in the presence of 0.08M NaNO₃ and 0.3M NaOH (b).

The starting, alkaline suspensions containing 0.45M FeCl₂, 0.056M BaCl₂, 0.15M NaNO₃, and different concentrations of excess NaOH were subjected to autoclaving at 200, 250 or 300°C. Ferromagnetic, brownish precipitates, consisting of BaFe₁₂O₁₉ with or without α -Fe₂O₃, were formed at temperatures above 200°C, depending on the concentration of excess NaOH. The properties of typical BaFe₁₂O₁₉ samples found by XRD to consist only of

BaFe₁₂O₁₉ are given in Table 2. The values of magnetization at 10 kOe, M, ($1 \text{ emu/g} = 4 \pi \rho \cdot 10^{-4} \text{ T}$, where $\rho = 5.3$ is specific gravity), depend on the conditions for their formation,

Table 2. Properties of the Typical BaFe₁₂O₁₉ Sample Prepared by Autoclaving at Different Temperatures, T, of Aqueous Suspensions Containing 0.45M FeCl₂, 0.15M NaNO₃, 0.056M Ba(OH)₂ and Different Concentrations of Excess NaOH.

Sample	Excess NaOH/M	T/°C	M/emu g ⁻¹	Hc/kOe	S/m ² g ⁻¹
G	6.0	300	47	0.8	3.6
H	1.0	300	34	0.7	1.5
I	6.0	250	33	0.8	3.9
J	2.0	250	30	0.8	1.0
K	1.0	250	30	0.7	0.7
L	6.0	200	20	0.7	9.5

whereas the values of coercive force, Hc, are lower than those of the ones prepared in the presence of Fe (III) and depend slightly on the conditions. These BaFe₁₂O₁₉ samples were found by SEM to consist of hexagonal, platelike particles whose diameter was greater than those of the ones prepared in the presence of iron (III) and became small with increasing the concentration of excess NaOH at 0.056M Ba(II) (Fig. 3). Such low Hc values might have resulted from the extremely large sectional-shape anisotropy of each particle.

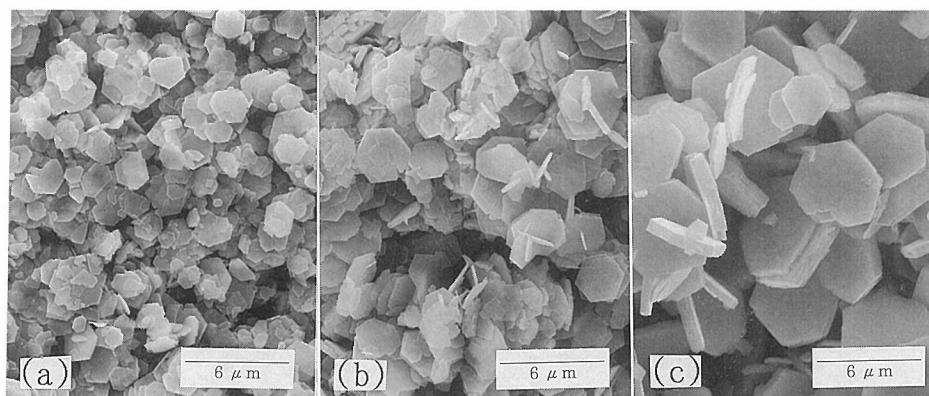


Fig. 3. SEM photographs of the BaFe₁₂O₁₉ samples G (a), I (b) and J (c).

In order to investigate the effects of the concentration of the total nitrates on the formation of BaFe₁₂O₁₉, suspensions containing 1.0M NaNO₃, 0.45M FeCl₂, 0.056M BaCl₂, and 6M excess NaOH were prepared and subjected to autoclaving at 250°C. The BaFe₁₂O₁₉ content in the products and their magnetic properties did not depend strongly on the nitrate concentration.

References

- (1) M. Kiyama, F. Kikui and T. Takada, *Bull. Inst. Chem. Res. Kyoto Univ.*, **65**, 187 (1987)
- (2) M. Kiyama, T. Kurata, T. Nakamura and T. Takada, *Bull. Inst. Chem. Res. Kyoto Univ.*, **68**, 275 (1991)
- (3) S. Nobuoka, and K. Ado, *Shiki-zai*, **60**, 265 (1987)
- (4) M. Kiyama, *Bull. Chem. Soc. Jpn.*, **49**, 1855 (1976)
- (5) M. Kiyama, T. Takada, N. Nagai, and N. Horiishi, in *Advance in Ceramics*, Vol. 15, p. 51, Am. Ceram. Soc., Coloumbus, Ohio (1986)
- (6) T. Sugimoto and E. Matijevic, *J. Colloid Interface Sci.*, **74**, 227 (1980)