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Air Oxidation of an Iron Powder Dispersed in Aqueous Solutions of Sodium Hydroxide

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A strongly alkaline, aqueous solution of NaOH in which an iron powder was well dispersed by mechanical stirring was oxidized at temperatures between 60 and 100°C by passing air into. The oxidation products were subjected to examinations by X-ray diffraction, scanning electron microscopic observation, and magnetic measurement at room temperature. Octahedral or hexahedral Fe₃O₄ particles with 1-5 μm in diameter were formed with or without concurrent formation of dislike α-Fe₂O₃ ones with 10-40 μm in diameter by oxidation and the formation rate of iron oxides increased remarkably with increases in the temperature from 80°C and in the NaOH concentration to 10M (M=mol/dm³). The presence of a slight amount of fine particles of α-Fe₂O₃ as a seed in the starting suspension accelerated the formation of α-Fe₂O₃ by oxidation at 10M NaOH and at 100°C.

KEY WORDS: Iron powder / Dislike α-Fe₂O₃ particle / Octahedral Fe₃O₄ particle / Air oxidation / Alkaline suspension

Introduction

When an iron powder dispersed in an acidic solution is oxidized at 80°C or below by blowing air into the suspension, a precipitate of α- or γ-FeO(OH) with or without iron oxides is formed.¹⁾ The precipitate formation by air oxidation proceeds at pH=4 while the iron powder remains in the suspension. It has been known that an iron(II) anion, [HFeO₂]⁻, where H₂O ligands are omitted, is formed in a strongly alkaline solution by dissolution of iron. The dissolution rate of iron in an aqueous NaOH solution was reported to become greater with increases both in the NaOH concentration and the temperature.²⁾ The air oxidation at temperatures between 60 and 100°C of an iron powder in aqueous NaOH solutions was carried out by varying the concentration of NaOH from 3 to 18M. This paper describes the conditions favorable for the formation of iron oxides by air oxidation.

Experimental

A cylindrical vessel with 18 cm in internal diameter and 50 cm in height made of stainless steel was used for the air oxidation experiments. It had in a central portion of the bottom an inlet neck with 2 cm in internal diameter closed with rubber stopper into which a

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glass tube with 0.15 cm in internal diameter had been inserted.

The air from which carbon dioxide had been removed by washing with a KOH solution was bubbled into the vessel from the glass tube at a rate not smaller than of 2 dm³/min. Each NaOH solution (4 dm³) of 3, 6, 10 or 18M was poured into the vessel and quickly heated to a desired temperature with an electric heater. After it had been reached, a crushed electrolytic iron powder (44.7g) with 74-140 μ m in particle size, which had been prepared by use of 100 and 200 mesh sieves, was poured, and dispersed with mechanical stirring at 330 rpm, and the flow rate of air was increased to 10 dm³/min. The oxidation at 60, 80 or 100°C was carried out for a fixed time of 5h. During the oxidation, conductivity water was supplied at frequent intervals into the suspension to keep 4 dm³ in the total volume. After the oxidation the suspension was cooled to room temperature.

The resulting products were separated by filtration, washed with water, and then dried at 60°C in air. The products were subjected to examinations by X-ray diffraction using FeK α radiation (XRD), scanning electron microscopic observation (SEM) and magnetization (M) at 10 kOe (1 kOe = $10^5/4\pi$ Am⁻¹) in a magnetic field using a vibrating-sample magnetometer. The Fe₃O₄ or α -Fe₂O₃ content was determined by comparing the relative intensities of XRD peaks of Fe₃O₄ d(311) 1.53, α -Fe₂O₃ d(104) 2.69 and Fe d(110) 1.01Å.

Results and Discussion

The contents of Fe₃O₄ and α -Fe₂O₃ in some typical samples obtained by the oxidation of the iron powder with 210 emu g⁻¹ in M (1 emu/g = $4\pi\rho 10^{-4}$ T, where ρ is specific gravity) are shown in Table 1, together with their M values. Fe₃O₄ particles are formed with or with-

Table 1. Products obtained by oxidation of alkaline suspensions containing the iron powder (11.2g/dm³)

Sample	NaOH/M	T/°C	Contents		M /emu g ⁻¹
			α -Fe ₂ O ₃	Fe ₃ O ₄	
A	18	100	0	0.50	149
B	10	100	0.47	0.48	59
C	6	100	0.23	0.49	112
D	3	100	0	0.16	193
E	10	80	0.04	0.63	126
F	10	60	0	0.05	202

out concurrent formation of α -Fe₂O₃ ones in the suspension by the air oxidation. The content of the total iron oxides in the oxidation products increases with increases both in the oxidation temperature from 80°C and in the NaOH concentration to 10M. A further increase in the NaOH concentration from 10M retards the formation of iron oxides, probably because of decreasing uniformity in the dispersion of iron particles with an increase in the viscosity of the suspension. The sample B consists of octahedral Fe₃O₄ particles and disclike α -Fe₂O₃ ones with 1-5 μ m and 10-30 μ m, respectively, in diameter (Fig. 1).

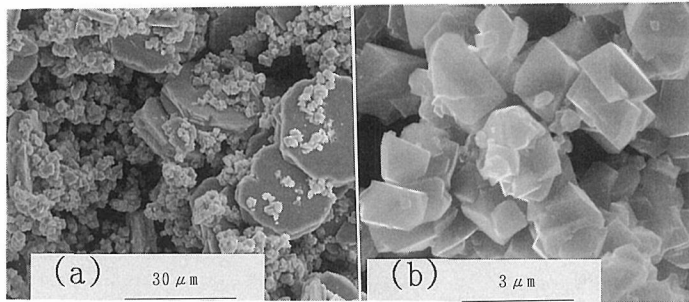


Fig. 1. SEM photographs of the sample B(a), enlargement of (a) showing detail of Fe_3O_4 particles(b).

Similar experiments were carried out by decreasing the air flow rate from $10 \text{ dm}^3/\text{min}$ to 5 and $2 \text{ dm}^3/\text{min}$, the other conditions being the same with those where the sample B had been obtained. The content of the total iron oxides in the oxidation products did not depend on the decrease of flow rate down to $2 \text{ dm}^3/\text{min}$.

In order to investigate the effects of the amount of iron powder added and of the stirring rate (SR) on the formation of iron oxides, experiments were carried out under the same conditions with those giving the sample B. As the amount of iron powder is increased, the formation rate of total iron oxides at 330 rpm becomes greater, the $\alpha\text{-Fe}_2\text{O}_3$ content depending on the amount of iron powder (Table 2). When the SR was decreased from 200 rpm, the content of the total iron oxides in the products decreased.

Table 2. Products obtained under the same conditions with those giving the sample B by varying the amount of the iron powder present in 10M NaOH

Sample	Fe powder /g dm^{-3}	Contents		M /emu g^{-1}
		$\alpha\text{-Fe}_2\text{O}_3$	Fe_3O_4	
G	2.8	0	0.05	190
H	5.6	0.07	0.74	164
I	22.4	0.17	0.80	77
J	44.8	0.08	0.83	106

Under the same oxidation conditions with those giving in sample B, several samples were prepared. The $\alpha\text{-Fe}_2\text{O}_3$ content in the products was sometimes found to decrease probably because of slight differences in the conditions, but without remarkable change in the content (90-95 wt%) of the total iron oxides. In the course of each oxidation, several portions of 100 cm^3 suspension were taken. The content of the total iron oxides in the products increased during the initial period of 3h and then became constant.

The fine iron powder (48 or 96g) with particle size below $46 \mu\text{m}$, which had been prepared by use of 325 mesh sieve, was oxidized under the same conditions with those giving the sample B by varying the SR. In these experiments, the Fe_3O_4 particles were found to be

formed without the formation of α -Fe₂O₃ ones. With the increase in the amount of the fine iron powder added, the formation of Fe₃O₄ particles is accelerated at 330 rpm. In the presence of constant amount of the fine iron powder (11.2g/dm³), the formation rate of Fe₃O₄ irregularly depends on the SR (Table 3). With the present reaction vessel the SR favorable for the formation of iron oxides depends on the amount and size of iron particles added.

Table 3. Products consisting of Fe₃O₄ and Fe obtained in the presence of the fine iron powder (below 45 μ m) under the same conditions with the sample B by varying the stirring rate (SR)

Sample	Fe powder /g dm ⁻³	SR /rpm	Fe ₃ O ₄ Content	M /emu g ⁻¹
K	11.2	330	0.31	147
L	22.4	330	0.70	101
M	11.2	110	0.76	103
N	11.2	60	0.52	123

As described above, the Fe₃O₄ particles are formed with or without concurrent formation of α -Fe₂O₃ ones depending on the oxidation conditions. It seemed that it would be possible to obtain the product consisting only of Fe₃O₄ or α -Fe₂O₃ particles under the conditions for the formation of a mixture of Fe₃O₄ and α -Fe₂O₃, provided that fine particles of Fe₃O₄ or α -Fe₂O₃ exist as seeds at the initial stage of oxidation. In order to examine this assumption, the Fe₃O₄ and α -Fe₂O₃ powders consisting of spherical particles with 0.18 μ m in diameter, which was estimated from the BET surface area ($S = 6.3\text{m}^2/\text{g}$), were selected as seeds from the samples which had been prepared from Fe(OH)₂ suspensions by air oxidation at 70°C^{3,4)} and transformed from Fe₃O₄ into α -Fe₂O₃ by heat treatment in air. Experiments were carried out by using the NaOH solutions containing slight amounts of Fe₃O₄ or α -Fe₂O₃ particles under the conditions giving the sample B. The results indicated that the presence of Fe₃O₄ seed (1.1g/dm³) did not promote the formation of Fe₃O₄ by oxidation, whereas the presence of slight amounts (0.4-1.6 g/dm³) of α -Fe₂O₃ seed remarkably accelerated the formation of α -Fe₂O₃, the mean diameter of the resulting α -Fe₂O₃ particles decreasing with increasing in the amount of the seed (Fig. 2).

Similar experiments were carried out with fine needlelike α -Fe₂O₃ particles with 0.5 μ m in length and fine hexagonal platelike with 1 μ m in diameter in place of the spherical ones. The needlelike particles were prepared by thermal decomposition at 400°C in air of α -FeO(OH), whereas the hexagonal platelike ones were prepared by autoclaving at 300°C an alkaline suspension of iron (III) hydroxide.⁵⁾ The shape and size of the α -Fe₂O₃ particles formed by oxidation in the presence of the α -Fe₂O₃ seed were also found to be governed by the shape and size of the α -Fe₂O₃ seed besides the amount (Fig. 3).

The formation of the iron oxides is considered to take place by the oxidation of [HFeO₂]⁻ formed by dissolution of iron particles. When the iron particles are well dispersed, [HFeO₂]⁻ consumed by oxidation to form Fe₃O₄ or α -Fe₂O₃ is incessantly replenished by dissolution of iron particles. In the present oxidation experiments the formation rate of the iron oxides must be considered to be mainly determined by the dissolution rate of iron particles in the alkaline medium. The α -Fe₂O₃ content in the oxidation product prepared in the

absence of α -Fe₂O₃ seed might be determined by the ratio of α -Fe₂O₃ nuclei to Fe₃O₄ ones formed at the initial stage of oxidation.

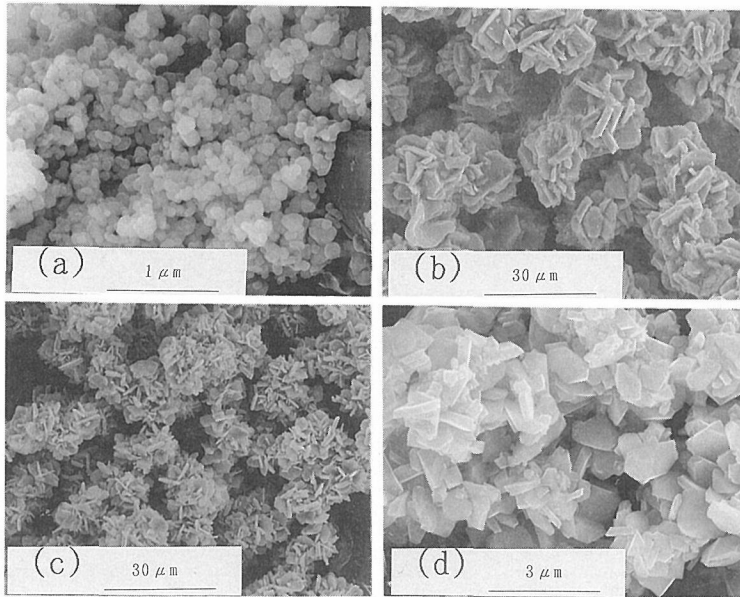


Fig. 2. SEM photographs of α -Fe₂O₃ particles, prepared in the presence of 0.4 (b), 0.8 (c) and 1.6g/dm³ (d) α -Fe₂O₃ seed (a).

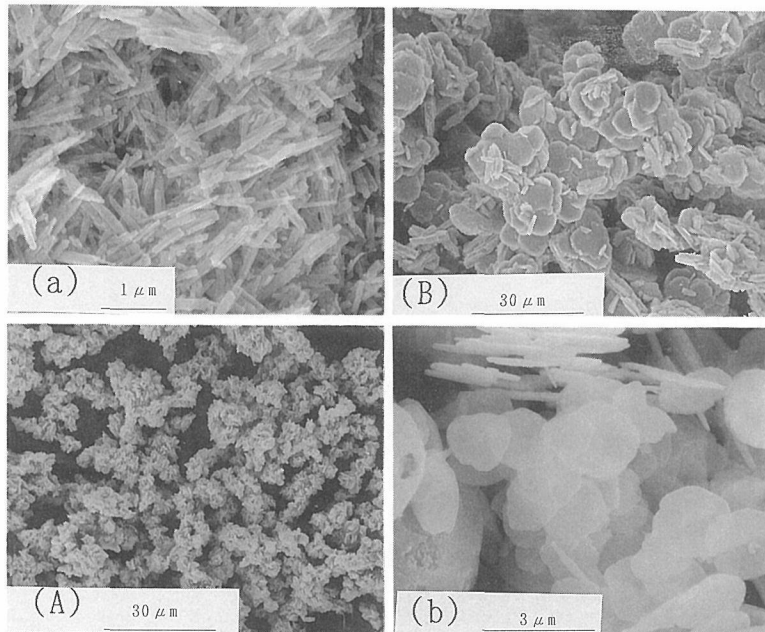


Fig. 3. SEM photographs of α -Fe₂O₃ particles (A) and (B), prepared in the presence of 0.8g/dm³ α -Fe₂O₃ seeds (a) and (b), respectively

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