

Formation of iron oxides by the oxidation of iron in Fe–MOH–H₂O and Fe–MOH–H₂O–O₂ systems (M = Li, Na, K)

S. UCHIDA, H. KASHIWAGI, T. SATO*, A. OKUWAKI

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai 980, Japan

The oxidation behaviours of iron powders, ca. 100 μm in diameter, in 5–50 *m* NaOH, 5–40 *m* KOH and 5–40 *m* LiOH solutions at 373–573 K were investigated in the absence and presence of oxygen, where *m* is molality. The oxidation of iron proceeded noticeably above 423 K to form Fe₃O₄, α-Fe₂O₃, α-NaFeO₂, γ-Fe₂O₃, Li_xFe_{3-x}O₄ and α-LiFeO₂ depending on the reaction conditions. The rate of oxidation in LiOH solutions was much slower than those in NaOH and KOH solutions.

1. Introduction

Many studies have been carried out on the hydrothermal oxidation of iron, primarily because it is important to study the corrosion behaviour of steels [1–7]. Recently, it has received attention for the application to hydrothermal synthesis of iron oxides possessing excellent magnetic property, dielectric property, corrosion resistance, etc., since it is possible to form iron oxides without alkali consumption for neutralization. It may be expected that various kinds of iron compounds such as Fe₃O₄, α-Fe₂O₃, γ-Fe₂O₃, Na₂FeO₂, LiFeO₂, LiFe₅O₈, etc. are formed by the oxidation of iron in caustic alkaline solutions. The crystalline phases and morphologies of iron compounds significantly depend on the reaction conditions, such as temperature, pH, coexisting ion, etc. Hirano and Somiya [8] reported the formation of octahedral and dendritic crystals of magnetite by the oxidation of iron in 10 *m* sodium hydroxide at 250–700 °C, where *m* is molality. On the other hand, in a previous study [9, 10] we reported the formation of micaceous iron oxide (α-Fe₂O₃), magnetite (Fe₃O₄), and α-NaFeO₂ by the oxidation of iron with oxygen in concentrated sodium hydroxide solutions at elevated temperatures. The details of the reactions, however, have not yet been clarified. In the present study, phase compositions of the products formed by the oxidation of iron powders in various alkaline solutions in the absence and presence of oxygen were investigated.

2. Experimental procedure

The reagent grade reduced iron powder of mean particle size of about 100 μm, was used as starting material. Sodium hydroxide, potassium hydroxide and lith-

ium hydroxide were of reagent grade and were used without further purification. Hydrothermal oxidation of iron powders in the presence of pressurized oxygen was conducted in a SUS 316 type stainless steel autoclave of 300 cm³ 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: three grams of reduced iron powder, 50 g of water and 10–150 g of sodium hydroxide, potassium hydroxide and lithium hydroxide were placed into a Teflon cup contained in an autoclave, and then the autoclave was sealed. After purging with nitrogen gas, the autoclave was heated in an electric furnace at about 6 °C min⁻¹ to a desired temperature under saturated vapour pressure, followed by injecting oxygen gas into the autoclave up to 5 MPa oxygen partial pressure to start oxidation. During the reaction period, the suspensions were agitated at the rate of 1200 r.p.m. and the oxygen partial pressure was kept at 5 MPa. After maintaining the desired temperature for 2 h, the autoclave was removed from the electric furnace and cooled quickly in air. On the other hand, the oxidation of iron powder in the absence of oxygen was conducted in a 20 cm³ 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 sodium hydroxide, potassium hydroxide and lithium hydroxide into the tube reactor, the tube was placed in a silicone oil bath set at a desired temperature and maintained for the desired time, then cooled quickly with water.

The reaction products were taken out and separated centrifugally, rinsed with methanol and dried at

* Author to whom correspondence should be addressed. *Present address:* Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-77, Japan.

105 °C for 12 h. The crystalline phases of the products were determined by X-ray powder diffraction analysis (XRD) using Fe-filtered CoK_α radiation.

3. Results and discussion

3.1. Oxidation in sodium hydroxide solutions

X-ray powder diffraction patterns of the precipitates obtained by the hydrothermal oxidation of iron powders in different concentrations of sodium hydroxide solutions at 573 K in the absence of oxygen for 2 h are shown in Fig. 1.

Hydrothermal oxidation of iron proceeded noticeably above 423 K under the present reaction conditions. Fe₃O₄ was the only product in 20 and 40 m NaOH solutions, as was shown by Hirano and Somiya [8]. On the other hand, α-NaFeO₂ was formed in 50 m NaOH solution. This is the first report of the formation of α-NaFeO₂ by the hydrothermal oxidation of iron, without oxygen. No formation of α-Fe₂O₃ could be observed under the present experimental conditions. According to these results, and the knowledge that divalent iron is soluble in concentrated sodium hydroxide solution [2] as FeO₂²⁻, the hydrothermal oxidation of iron in sodium hydroxide solution may be expressed as follows

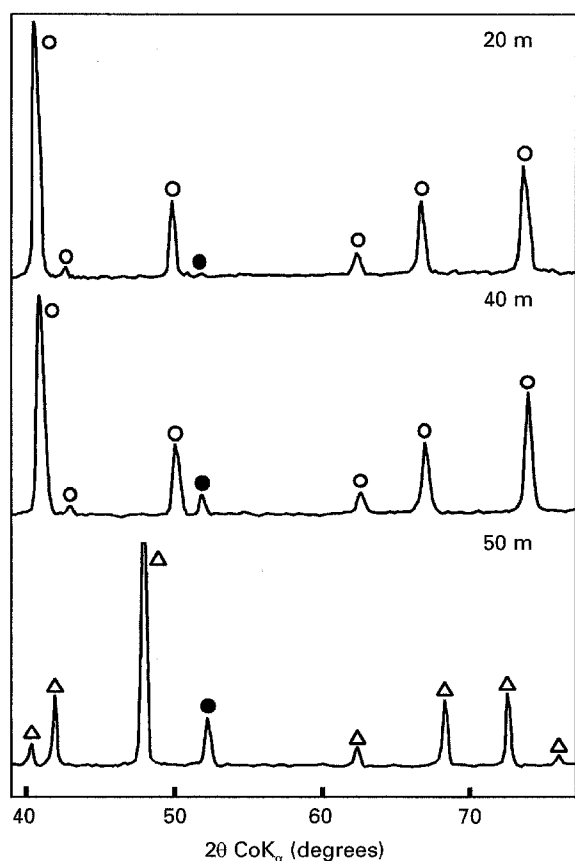
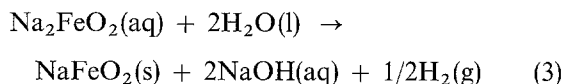
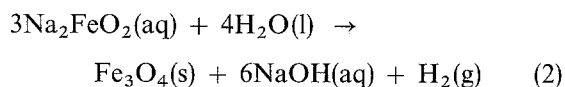


Figure 1 X-ray powder diffraction patterns of the precipitates obtained by the hydrothermal oxidation of iron powders in various concentrations of sodium hydroxide solutions at 473 K in the absence of oxygen for 2 h. ● α-Fe; ○ Fe₃O₄; △ α-NaFeO₂.



The oxidation rate of iron seemed to decrease with increasing sodium hydroxide concentration, since the peak intensity of iron used as starting materials increased with increasing sodium hydroxide concentration. It may be due to the increase of the viscosity of the solution and/or depression of Reactions 2 and 3 by decreasing the activity of H₂O.

Phase compositions of the precipitates obtained by the oxidation of iron powders in various concentrations of sodium hydroxide solutions at various temperatures and (a) 0 and (b) 5 MPa oxygen for 2 h are shown in Fig. 2(a) and (b), respectively.

Oxidation of iron became noticeable above 423 K, both in the absence and presence of oxygen. In the absence of oxygen, Fe₃O₄ and α-NaFeO₂ were formed in 10–40 m NaOH above 423 K, and in 50 m NaOH above 473 K, respectively. On the other hand,

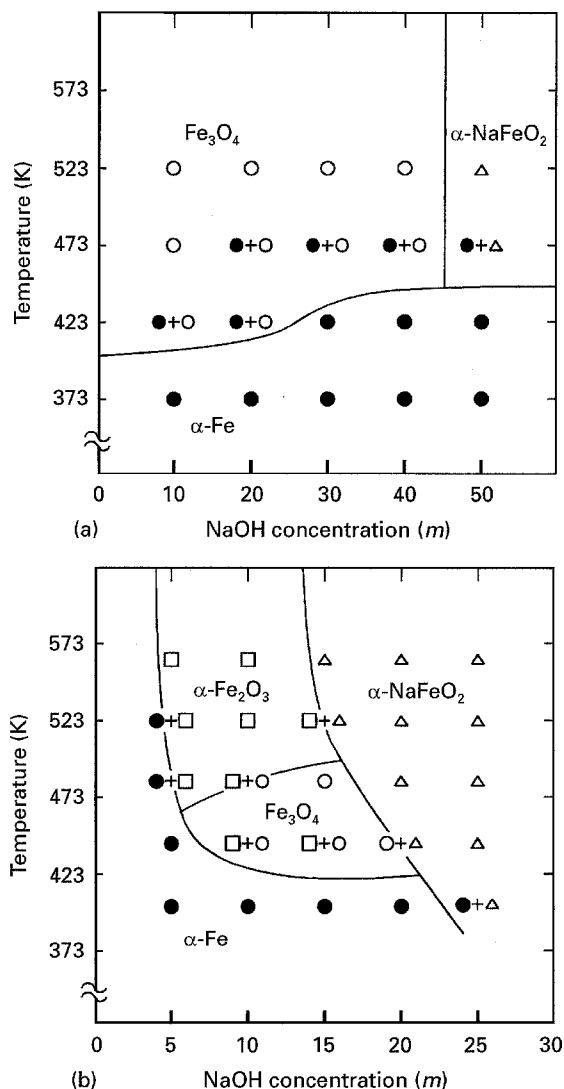
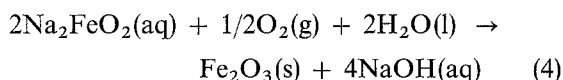
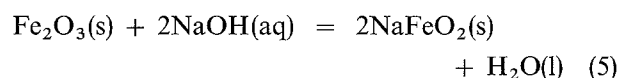


Figure 2 Phase composition of the precipitates obtained by the oxidation of iron powders in various concentrations of sodium hydroxide solutions at various temperatures and (a) 0 and (b) 5 MPa oxygen. ● α-Fe; ○ Fe₃O₄; △ α-NaFeO₂; □ α-Fe₂O₃.

in the presence of 5 MPa oxygen, α -Fe₂O₃ was also formed together with Fe₃O₄ and α -NaFeO₂. The formation of α -Fe₂O₃ may be expressed as



It is seen that the critical concentration of sodium hydroxide above which α -NaFeO₂ is formed significantly decreased in the presence of oxygen. In a previous study [9], it was confirmed that the critical sodium hydroxide concentrations observed in the presence of oxygen were in good agreement with those thermodynamically calculated for the equilibrium expressed by Reaction 5



3.2. Oxidation in potassium hydroxide solutions

The phase compositions of the precipitates obtained by the oxidation of iron powder in various concentra-

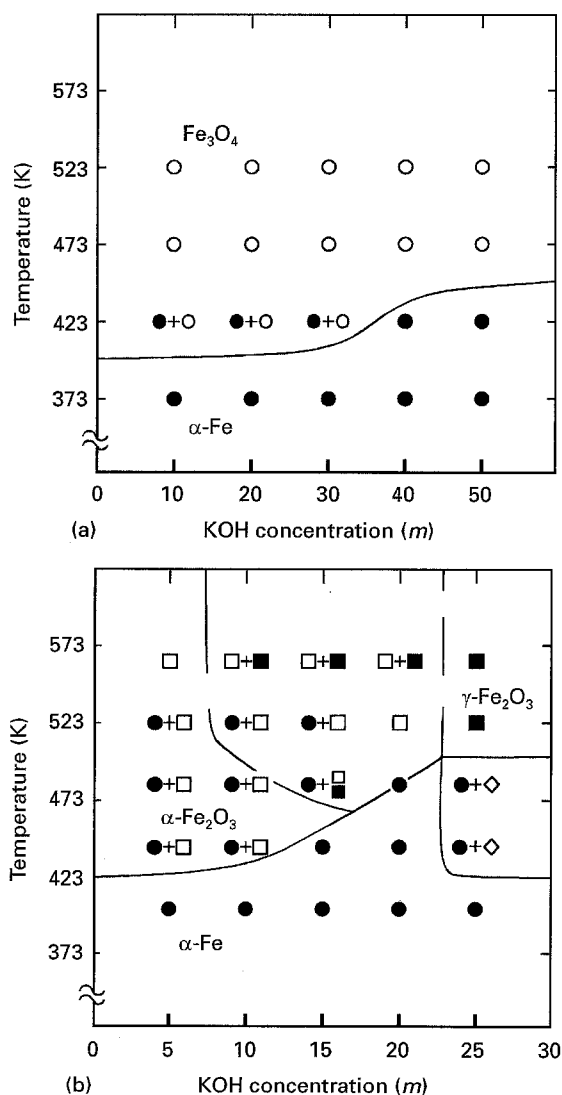


Figure 3 Phase compositions of the precipitates obtained by the oxidation of iron powder in various concentrations of potassium hydroxide solutions at various temperatures and (a) 0 and (b) 5 MPa oxygen. ● α -Fe; ○ Fe₃O₄; □ α -Fe₂O₃; ▲ γ -Fe₂O₃; ◇ unknown.

tions of potassium hydroxide solutions at various temperatures and (a) 0 and (b) 5 MPa oxygen for 2 h are shown in Fig. 3(a) and (b), respectively.

The oxidation behaviours of iron in potassium hydroxide solutions in the absence of oxygen was similar to those in sodium hydroxide solutions, i.e. the oxidation proceeds noticeably above 423 K, and Fe₃O₄ was formed in 10–40 m KOH solutions. On the other hand, in the presence of oxygen α -Fe₂O₃ was formed in 5–20 m potassium hydroxide solutions above 423 K, whereas γ -Fe₂O₃ and an unknown compound were formed in 25 m KOH solutions above 523 K and below 473 K, respectively. Direct formation of γ -Fe₂O₃ in potassium hydroxide solution is new and study of the details of the reaction is now in progress.

3.3. Oxidation in lithium hydroxide solutions

Phase compositions of the precipitates obtained by the oxidation of iron powder in various concentrations of lithium hydroxide solutions at various temperatures and (a) 0 and (b) 5 MPa oxygen for 2 h are shown in Fig. 4(a) and (b), respectively.

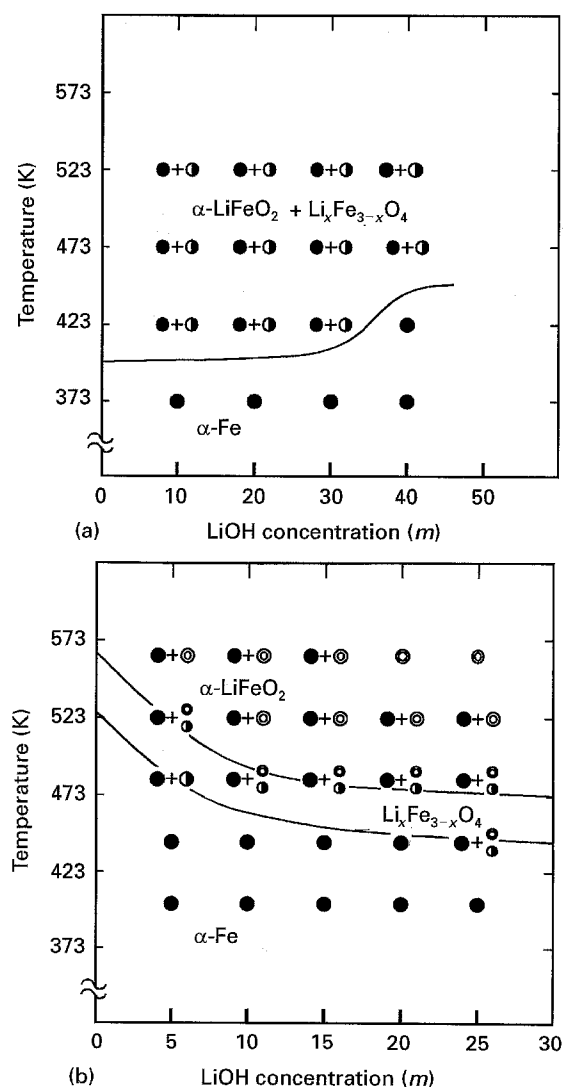


Figure 4 Phase compositions of the precipitates obtained by the oxidation of iron powder in various concentrations of LiOH solutions at various temperatures and (a) 0 and (b) 5 MPa oxygen. ● α -Fe; ● $\text{Li}_x\text{Fe}_{3-x}\text{O}_4$; ⊕ α -LiFeO₂.

The oxidation of iron proceeded noticeably above 423 K. Since iron used as starting material remained, even at 573 K, it might be concluded that the oxidation rate of iron in lithium hydroxide solution was much slower than those in sodium hydroxide and potassium hydroxide solutions. The reaction product in the absence of oxygen was magnetite alloyed with Li^+ , $\text{Li}_x\text{Fe}_{3-x}\text{O}_4$. On the other hand, in the presence of oxygen, the mixtures of $\text{Li}_x\text{Fe}_{3-x}\text{O}_4$ and $\alpha\text{-LiFeO}_2$ were formed at low temperature, and $\alpha\text{-LiFeO}_2$ as single phase at high temperature. These results suggest that $\text{Li}_x\text{Fe}_{3-x}\text{O}_4$ is oxidized to $\alpha\text{-LiFeO}_2$ in the presence of oxygen.

Time dependence of (a) the peak intensity ratio of $I[\text{Li}_x\text{Fe}_{3-x}\text{O}_4(400)] / \{I[\text{Li}_x\text{Fe}_{3-x}\text{O}_4(400)] + I[\text{Fe}(110)]\}$ and (b) lattice parameter of $\text{Li}_x\text{Fe}_{3-x}\text{O}_4$ for the products obtained in 2 m LiOH solutions at 523 K in the absence of oxygen is shown in Fig. 5(a) and (b), where $I[\text{Li}_x\text{Fe}_{3-x}\text{O}_4(400)]$ and $I[\text{Fe}(110)]$

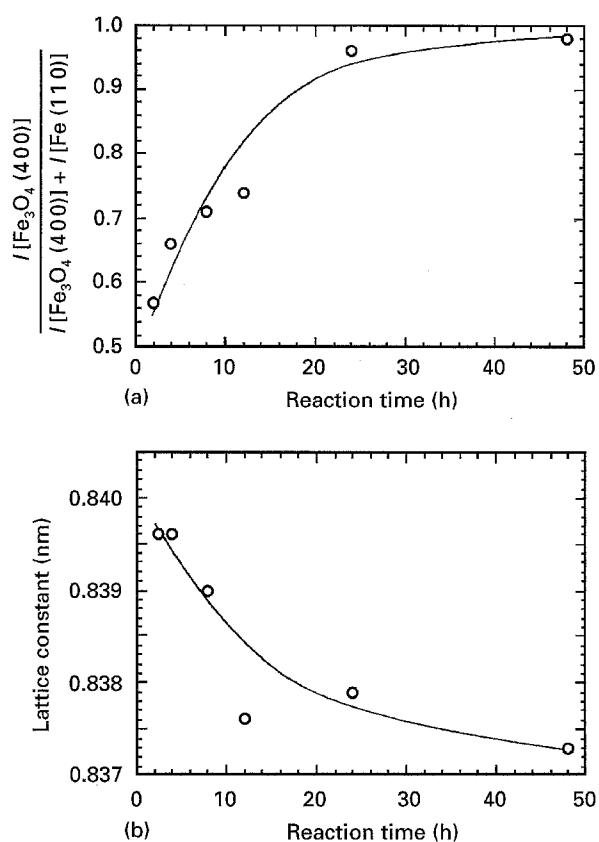


Figure 5 Time dependence of (a) the peak intensity ratio of $I[\text{Li}_x\text{Fe}_{3-x}\text{O}_4(400)] / \{I[\text{Li}_x\text{Fe}_{3-x}\text{O}_4(400)] + I[\text{Fe}(110)]\}$ and (b) lattice constant of $\text{Li}_x\text{Fe}_{3-x}\text{O}_4$ for the products obtained in 2 m LiOH solutions at 523 K in the absence of oxygen.

are the peak intensity of (400) of $\text{Li}_x\text{Fe}_{3-x}\text{O}_4$ and (100) of $\alpha\text{-Fe}$, respectively.

The peak intensity ratio increased with time and it was seen that the oxidation of $\alpha\text{-Fe}$ to $\text{Li}_x\text{Fe}_{3-x}\text{O}_4$ was almost completed for 50 h. The lattice constant for 1 h, $a = 0.8396$ nm, was exactly identical to that of stoichiometric Fe_3O_4 [11], but decreased to 0.8373 nm for 50 h, indicating that Fe_3O_4 is alloyed with Li^+ . By assuming Vegard's law for the lattice constant of Fe_3O_4 and $\alpha\text{-Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($a = 0.8331$ nm) [12], the precipitate for 50 h was suspected to be $\text{Li}_{0.18}\text{Fe}_{2.82}\text{O}_4$. The amount of Li^+ alloyed was close to that in lithium ferrite formed by electrochemical reaction in 4 m LiOH solution at 30 °C [16].

4. Conclusions

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

1. Various iron compounds, Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-NaFeO}_2$, $\gamma\text{-Fe}_2\text{O}_3$, $\text{Li}_x\text{Fe}_{3-x}\text{O}_4$ and $\alpha\text{-LiFeO}_2$ were formed by the oxidation of iron powder in 5–50 m NaOH, 5–40 m KOH and 5–40 m LiOH solutions in the presence and absence of oxygen.
2. The rate of oxidation in lithium hydroxide solution was much slower than those in sodium hydroxide and potassium hydroxide solutions.

References

1. D. M. DRAZIC and S. C. HAO, *Electrochim. Acta* **27** (1982) 1409.
2. F. BECK, R. KAUS and M. OBRST, *Ibid.* **30** (1985) 173.
3. J. ZOU and D. CHIN, *Ibid.* **32** (1987) 1751.
4. V. S. MURALIDHARAN and M. VEERASHANMUGAMANI, *J. Appl. Electrochem.* **15** (1985) 675.
5. J. ZOU and D. CHIN, *Electrochim. Acta* **33** (1988) 477.
6. G. LARRAMONA and C. GUTIERREZ, *J. Electrochem. Soc.* **136** (1989) 2171.
7. S. ZECEVIC, D. M. DRAZIC and S. GOJKOVIC, *Electrochim. Acta* **36** (1991) 5.
8. S. HIRANO and S. SOMIYA, *J. Crystal Growth* **35** (1976) 273.
9. S. UCHIDA, T. SATO and A. OKUWAKI, *J. Mater. Sci.* **27** (1992) 1332.
10. S. UCHIDA, T. SATO and A. OKUWAKI, *J. Chem. Tech. Biotechnol.* **57** (1993) 221.
11. JCPDS 19-629.
12. JCPDS 38-259.
13. Y. MATSUMOTO and J. HOMBO, *J. Electroanal. Chem.* **279** (1990) 331.

Received 1 December 1994

and accepted 13 February 1996