

Reduction of haematite to magnetite under controlled hydrothermal conditions with hydrogen gas

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Haematite ($\alpha\text{-Fe}_2\text{O}_3$) was reduced to magnetite (Fe_3O_4) under hydrothermal conditions, by the use of an autoclave into which hydrogen gas was able to be admitted. The stable reduced conditions for magnetite precipitation were produced even at 100°C . In acid and neutral mineralizers, the rate of haematite reduction was small below 300°C and increased with an increase in reaction temperature above 300°C . Magnetite crystals obtained in these solutions were large and faceted octahedrons in shape. Alkaline mineralizers except NaOH solution accelerated the reduction at low temperatures below 300°C and gave small magnetite crystals. The reduction of haematite to magnetite was completed even at 150°C in concentrated CsOH solution (1.0 mol l^{-1}).

1. Introduction

It has been interested in controlling the environment under hydrothermal conditions, because the oxidation potential plays an important role in hydrothermal systems to synthesize compounds in which elements are capable of appearing in various oxidation states [1]. Haematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) are naturally occurring minerals of iron oxides with different oxidation states. Crystals of magnetite were obtained from metallic iron or haematite under a reducing environment by hydrothermal methods [2-6]. The reducing condition was generated by hydrogen produced by reaction of iron or reactor vessel with water [2-5], and by carbon monoxide produced by decomposition of formic acid [6]. These methods depended on gas formation to provide the stable condition for magnetite precipitation, so that the desired conditions were obtained only above 250°C [5, 6]. In some cases, it was difficult to maintain the reducing condition because hydrogen diffused out from the hydrothermal system through capsule or autoclave wall [2-4].

The authors have developed an autoclave into which a gas can be admitted to control the environment in reaction chamber. The desired environment is generated even at room temperature and is maintained by supplement of the gas, if necessary. In the present work, hydrothermal reduction of haematite to magnetite was investigated as an example to synthesize oxides of low cation valences under the controlled reducing atmosphere with coexistence of hydrogen gas by the use of the autoclave. The effect of mineralizers on the reduction of haematite was also studied.

2. Experimental procedure

The autoclave used in this study is shown in Fig. 1. It

was made of carburized steel with a liner of Inconel-600 (nickel alloy). A high pressure valve was attached to the autoclave to admit a gas into the reaction chamber (12.8 cm^3) to control the environment.

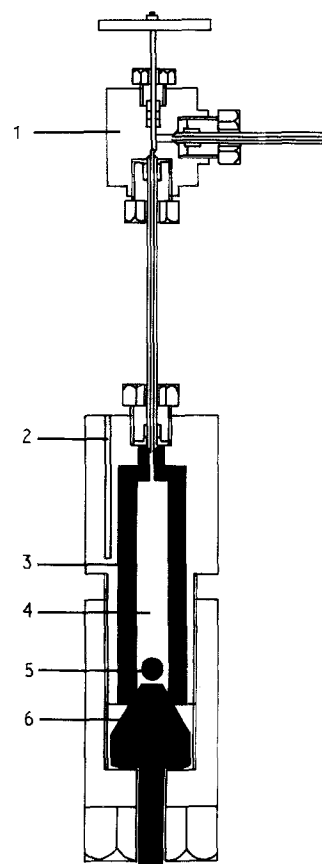


Figure 1 Autoclave for controlling environment under hydrothermal conditions. 1. high pressure valve, 2. thermocouple well, 3. liner, 4. reaction chamber, 5. ball for agitation, 6. cone.

The starting haematite powder ($\alpha\text{-Fe}_2\text{O}_3$) was procured from Wako Pure Chem. Ind. Ltd. Mineralizer solutions (0.1 to 1.0 mol l^{-1}) were prepared from reagents (NaCl , NaNO_3 , HCl , NH_4Cl , HNO_3 , NH_4NO_3 , NH_4OH , LiOH , NaOH , KOH , RbOH , CsOH) by dissolving in distilled water.

The haematite powder (0.5 g) and a mineralizer (5 ml) were put into the chamber of the autoclave together with a stirring ball made of Inconel-600. Then, hydrogen gas was admitted into the chamber up to 4.9 MPa through the high pressure valve from hydrogen gas bomb. The autoclave was heated up to 400°C at $40^\circ\text{C min}^{-1}$ by an induction heater, which was rocked back and forth $40 \text{ times min}^{-1}$ to agitate the contents of the chamber.

After hydrothermal treatment, the solid reaction products were filtered and dried in air at 75°C . They were identified by X-ray powder diffraction (Rigaku, RAD-RC) and observed by a scanning electron microscope (Hitachi, S-530). The magnetite content in the reaction products was determined by the relative values of magnetic susceptibility. After being weighed (about 50 mg), the reaction product in a quartz glass cell was vertically suspended by a quartz glass spring. When it was set in a constant magnetic field (magnetic flux density 0.03 Wb m^{-2} , determined by a flux meter), the stretched distance of the spring was measured to calculate the stretched distance per unit mass. The magnetite content was determined by dividing the stretched distance of the reaction product by that of pure magnetite, which was produced by hydrothermal reduction of haematite in pure water at 350°C for 2 h with 4.9 MPa hydrogen gas pressure and ascertained to be pure magnetite by X-ray powder diffraction. The magnetite content determined by this method agreed well with those determined from the relative intensity of X-ray diffraction.

3. Results and discussion

3.1. Reduction in pure water

The haematite powder was treated in pure water from 200 to 400°C for 30 min under different hydrogen pressures. The magnetite content in the reaction products is shown in Fig. 2. Any other compounds except haematite and magnetite were not detected by X-ray diffraction. Magnetite was not produced by hydrothermal treatment without hydrogen gas. It has been pointed out that haematite was in a stable phase in pure water up to 700°C [6, 7]. When hydrogen gas was admitted over 1.0 MPa , the haematite was completely reduced to magnetite at 400°C . High pressure of hydrogen gas slightly accelerated the reduction and a small amount of magnetite was produced even at 225°C .

The magnetite content in the reaction products were linearly increased with the reaction time (Fig. 3), which suggested that the rate of haematite reduction was constant under given conditions. The considerable rate-controlling reactions were as follows: (1) hydrogen diffusion in solution, (2) surface reaction (hydrogen or oxygen diffusion in reaction layer), (3) a haematite dissolution and magnetite deposition,

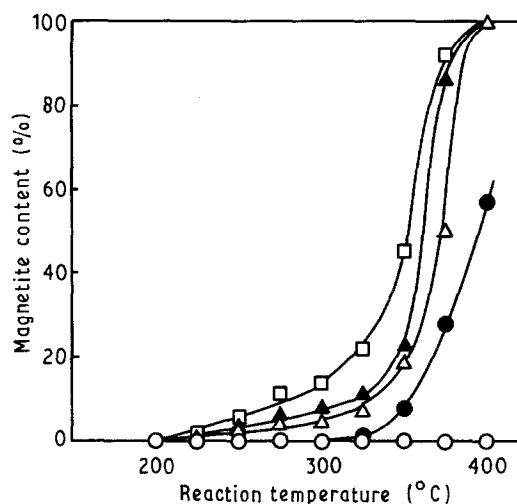


Figure 2 Magnetite contents plotted against reaction temperature at various hydrogen pressures. Reactions were carried out in H_2O for 30 min (\circ 0 MPa , \bullet 0.5 MPa , \triangle 1.0 MPa , \blacktriangle 2.9 MPa , \square 4.9 MPa).

(4) reduction of Fe^{3+} in solution. It was considered that hydrogen diffusion and reduction of Fe^{3+} in solution were relatively fast because the contents of the autoclave were agitated and hydrogen gas pressure was relatively high (4.9 MPa). Murata and Kasaoka [8] reported that the relation between the magnetite content and reaction time obtained by reduction of haematite in hydrogen gas described a parabola, and they concluded that oxygen diffusion was the rate-controlling reaction. The linear relation between magnetite content and reaction time obtained in this study did not agree that the rate-controlling reaction was diffusion in solid, but showed that it was "haematite dissolution and magnetite deposition", just like the crystal growth of magnetite. It was assumed that some of the ferric ions dissolved from haematite into a mineralizer solution were immediately reduced to ferrous ions and precipitated as magnetite, which was more stable than haematite under the reducing conditions employed in this study.

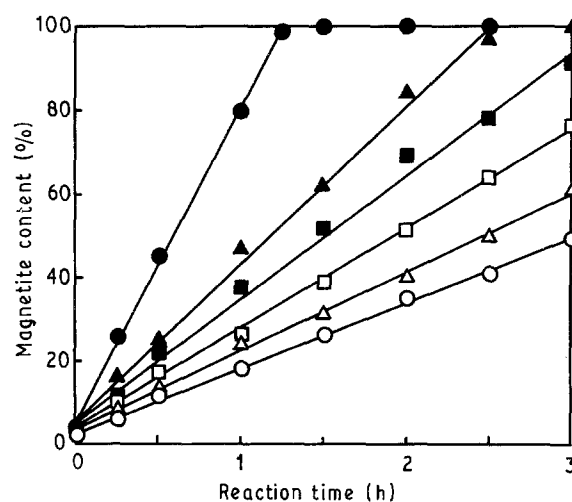


Figure 3 Magnetite contents plotted against reaction time at various temperatures in H_2O with 4.9 MPa hydrogen gas pressure (\circ 300°C , \triangle 310°C , \square 320°C , \blacksquare 330°C , \blacktriangle 340°C , \bullet 350°C).

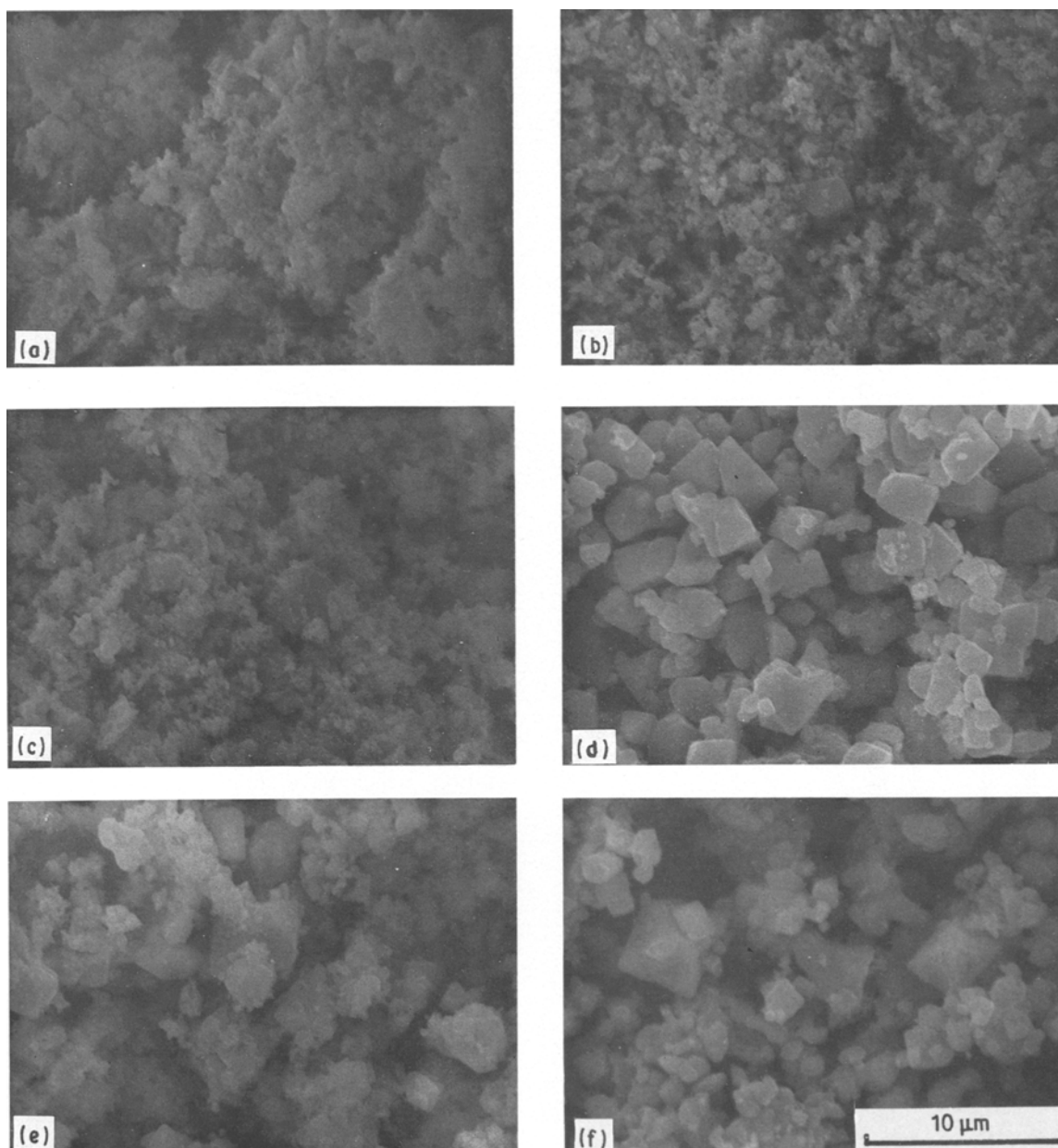


Figure 4 Photographs of reaction products in H_2O at 4.9 MPa hydrogen gas pressure. (a) starting haematite, (b) 300 °C, 30 min (magnetite contents; 12%), (c) 350 °C, 0.5 h (45%), (d) 400 °C, 0.5 h (100%), (e) 340 °C, 1.5 h (61%), (f) 340 °C, 2.5 h (100%).

Photographs of reaction products are shown in Fig. 4. Before the reduction was complete, small particles of the starting haematite under $0.5 \mu\text{m}$ were observed together with large particles of magnetite (Fig. 4b, 4c and 4e). The result suggested that the reduction of haematite proceeded by spontaneous nucleation and growth of magnetite.

3.2. Effect of mineralizer

The magnetite content in reaction products in various mineralizers, neutral (H_2O , NaCl , NaNO_3), acid (HCl , NH_4Cl , HNO_3 , NH_4NO_3) and alkaline (NH_4OH , LiOH , NaOH , KOH , RbOH , CsOH) solutions (0.1 mol l^{-1}), is shown in Fig. 5 against reaction temperature, and photographs of magnetite crystals synthesized in these solutions are shown in Fig. 6.

When solutions including nitrate ions (NaNO_3 , HNO_3 , NH_4NO_3) were used as mineralizer, ammonium ions were formed by reduction of nitrate ions.

Iron oxide is the well known catalyst for production of ammonia by the Harber–Bosch method, and it might have a catalytic effect on the reduction of nitrate ions to ammonium ions in solution. Formation of ammonium ions increased in pH value of these solutions and gave different curves of magnetite contents against reaction temperature from others in neutral and acid solutions.

In general, S-shaped curves in the relationship between magnetite content and reaction temperature, were obtained in neutral and acid solutions, and faceted large magnetite crystals were grown. Low magnetite content in these solutions at low temperature below 300 °C gave an assumption that the number of magnetite nuclei was small and growth rate of these nuclei was increased with the increase in reaction temperature above 300 °C. On the other hand, alkaline solutions accelerated the reduction of magnetite at low temperature from 200 to 250 °C, in comparison with neutral and acid solutions. The most effective

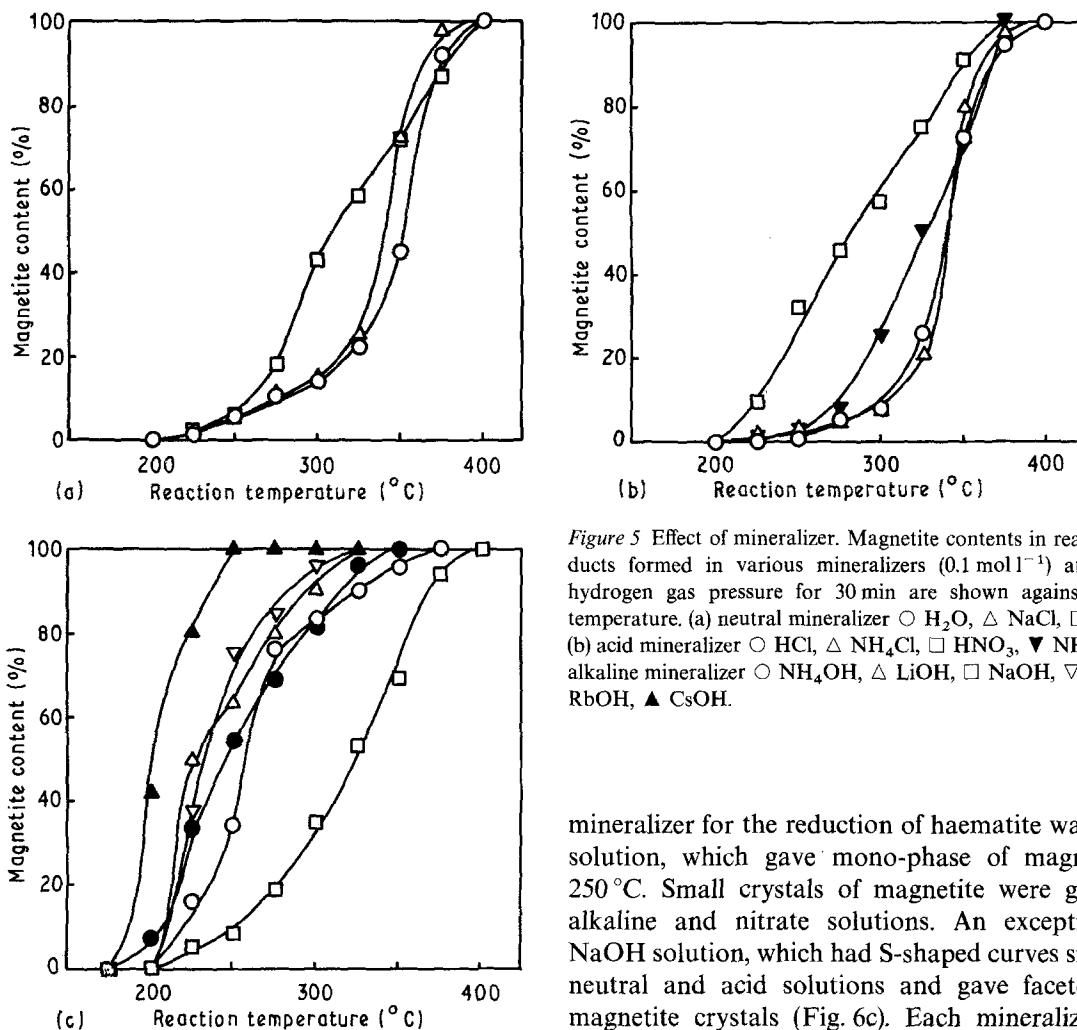


Figure 5 Effect of mineralizer. Magnetite contents in reaction products formed in various mineralizers (0.1 mol l^{-1}) at 4.9 MPa hydrogen gas pressure for 30 min are shown against reaction temperature. (a) neutral mineralizer $\circ \text{H}_2\text{O}$, $\triangle \text{NaCl}$, $\square \text{NaNO}_3$. (b) acid mineralizer $\circ \text{HCl}$, $\triangle \text{NH}_4\text{Cl}$, $\square \text{HNO}_3$, $\nabla \text{NH}_4\text{NO}_3$. (c) alkaline mineralizer $\circ \text{NH}_4\text{OH}$, $\triangle \text{LiOH}$, $\square \text{NaOH}$, ∇KOH , $\bullet \text{RbOH}$, $\blacktriangle \text{CsOH}$.

mineralizer for the reduction of haematite was CsOH solution, which gave mono-phase of magnetite at 250°C. Small crystals of magnetite were grown in alkaline and nitrate solutions. An exception was NaOH solution, which had S-shaped curves similar to neutral and acid solutions and gave faceted large magnetite crystals (Fig. 6c). Each mineralizer must

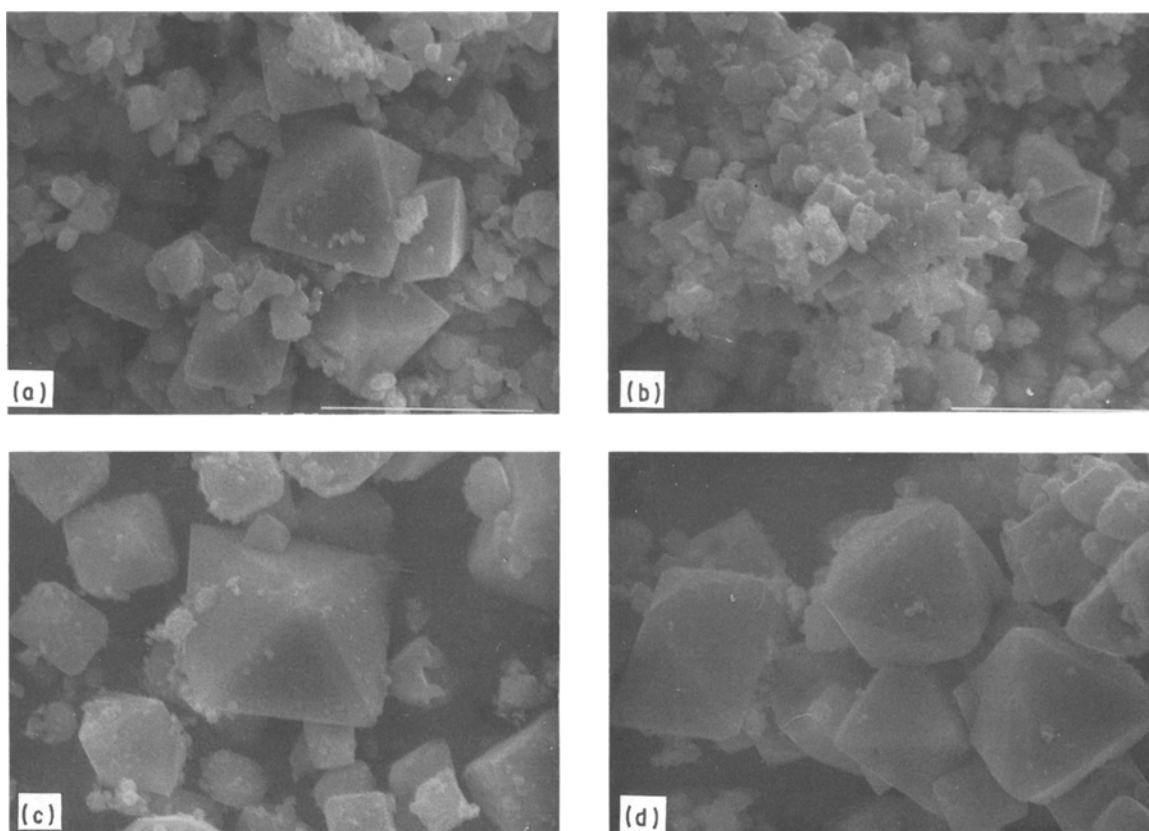


Figure 6 Photographs of magnetite crystals produced in various mineralizers (0.1 mol l^{-1}) at 400°C (except KOH, RbOH, CsOH solutions, at 350°C) under 4.9 MPa hydrogen gas pressure for 30 min. Neutral mineralizer (a) NaCl (b) NaNO₃, Acid mineralizer (c) HCl (d) NH₄Cl (e) HNO₃ (f) NH₄NO₃, Alkaline mineralizer (g) NH₄OH (h) LiOH (i) NaOH (j) KOH (k) RbOH (l) CsOH.

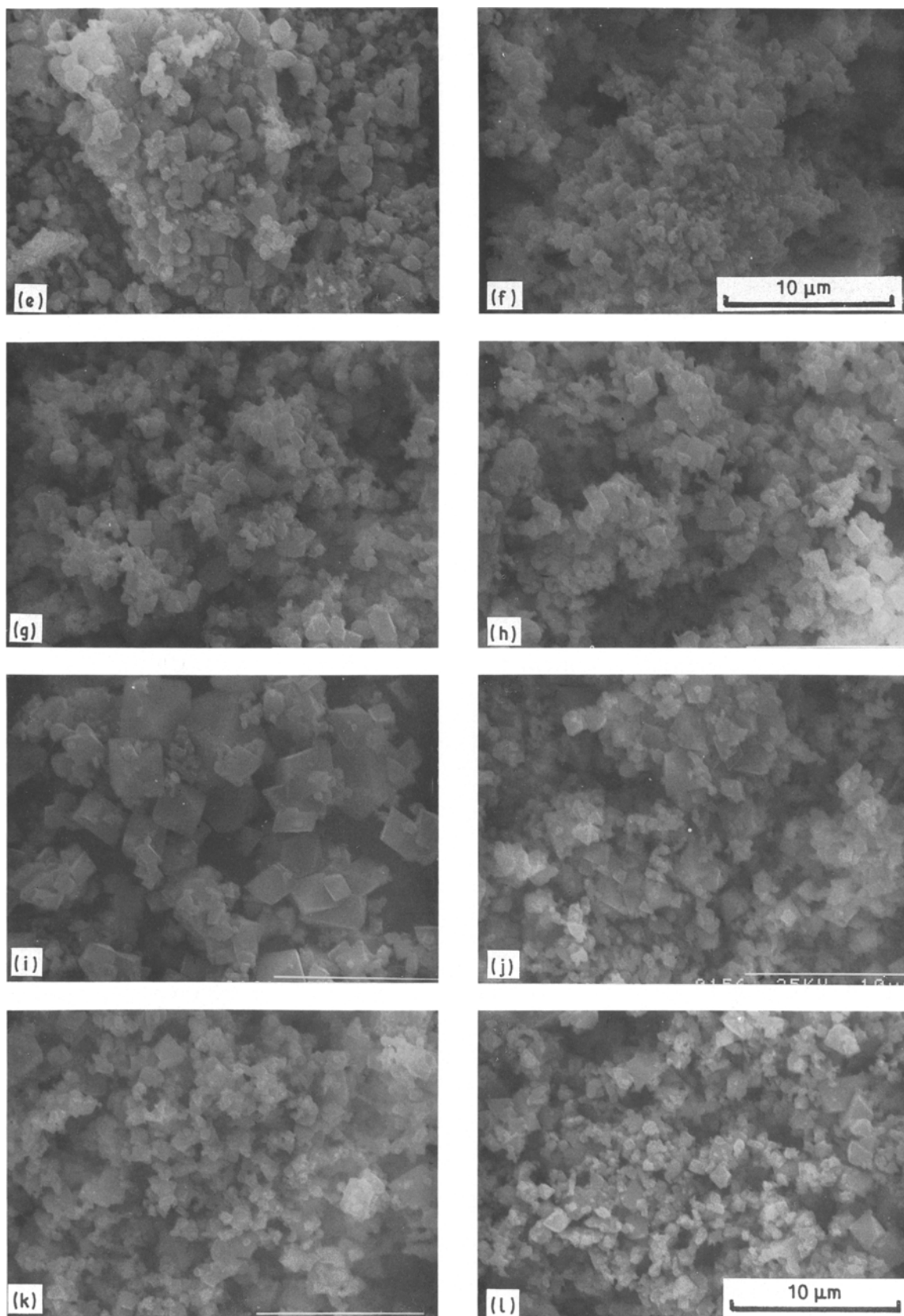


Figure 6 Continued.

have different solubility of haematite, which may cause the difference in reduction rate of haematite and morphology of the obtained magnetite crystals.

Mineralizers, which gave S-shaped curves of magnetite content against reaction temperature, seemed to be effective for crystal growth of magnetite. In fact, NaOH and NH_4Cl solutions have been used as mineralizers for crystal growth of magnetite [4, 5].

The increase in concentration of mineralizers shifted the curves of magnetite contents against reaction temperature to the low temperature region. Concentrated mineralizers with S-shaped curves, such as 0.5 mol l^{-1} NaOH solution, gave larger magnetite crystals (Fig. 7a). In CsOH solution with high concentration (1.0 mol l^{-1}), the reduction of haematite occurred even at 100°C . According to X-ray diffraction,

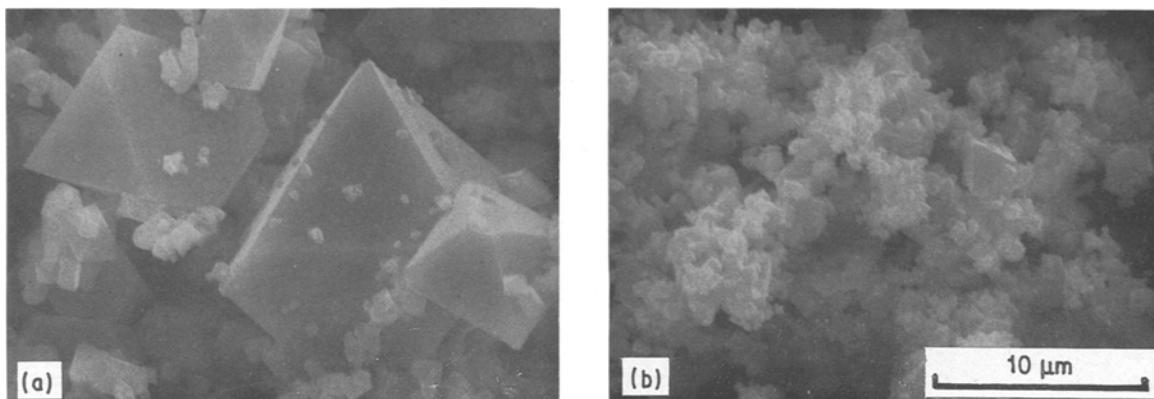


Figure 7 Photographs of magnetite crystals produced (a) in NaOH solution (0.5 mol l^{-1}) at 400°C for 30 min and (b) in CsOH solution (1.0 mol l^{-1}) at 150°C for 2 days under 4.9 MPa hydrogen gas pressure.

haematite was completely reduced to magnetite in the CsOH solution under hydrothermal conditions at 200°C and 4.9 MPa hydrogen pressure for 2 days, though magnetite crystals obtained were small (Fig. 7b).

4. Conclusion

Haematite was reduced to magnetite under hydrothermal conditions below 400°C with the controlled environment by hydrogen gas previously admitted into the reaction chamber, using various mineralizers. When solutions including nitrate ions were used as mineralizers, ammonium ions were formed by reduction of nitrate ions and pH value of these solutions was increased. In neutral and acid mineralizers, S-shaped curves were obtained in the relationship between magnetite content and reaction temperature, which meant that the rate of haematite reduction was small at low temperature below 300°C and increased with an increase in reaction temperature above 300°C . In these solutions, faceted large magnetite crystals were obtained. The reduction rate of haematite was constant under a given condition from 300 to 350°C in pure water with 4.9 MPa hydrogen gas pressure. The result suggested that the rate-controlling reaction of haematite reduction under hydrothermal conditions was dissolution of haematite into mineralizer

solution and deposition of magnetite, just like crystal growth of magnetite with constant growth rate. Alkaline mineralizers except NaOH solution accelerated the reduction at low temperatures from 200 to 250°C , in comparison with neutral and acid mineralizers, and gave small magnetite crystals. High concentration of mineralizers also accelerated the reduction. In CsOH solution (1.0 mol l^{-1}), haematite was completely reduced to magnetite even at 150°C .

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