Reduction of Titania–Ferrous Ore by Hydrogen

Eungyeul PARK and Oleg OSTROVSKI¹⁾

Former PhD Student, School of Materials Science and Engineering, University of New South Wales, Sydney 2052, Australia, now at Max-Planck-Institut für Eisenforschung, Max-Planck Str. 1, D-40237 Düsseldorf, Germany. E-mail: park@mpie.de

1) School of Materials Science and Engineering, University of New South Wales, Sydney 2052, Australia.

(Received on November 4, 2003; accepted in final form on February 16 2004)

The reduction of titania–ferrous ore (ironsand) containing 57.2 mass% of iron and 7–8 mass% of TiO₂ was investigated in isothermal experiments using H₂–Ar gas mixtures in a laboratory fixed bed reactor in the temperature range from 973 to 1373 K. The degree of reduction was measured using an on-line Dew Point sensor and the samples in the course of reduction were characterized using SEM and XRD analyses.

The complete reduction of iron oxide in the ore by 25vol% H₂–Ar was achieved within 60 min at temperature higher than 1123 K. At 1173 K, the reduction rate increased with hydrogen content in the reducing gas up to 25 vol% H₂. The composition of samples after 2-h reduction by 25vol% H₂–Ar depended on the reduction temperature. Below 1073 K, the final sample contained iron and iron–titanium oxides. At temperatures above 1173 K, the final sample was composed of iron and titanium oxide. The reduction path at temperatures above 1173 K is suggested as follows:

KEY WORDS: ironsand; titanomagnetite; reduction; hydrogen; reduction path.

1. Introduction

Among titania–ferrous iron ores found throughout the world, the ironsand from New Zealand is in a large deposit and contains about 57 mass% of total iron, with the price of about 2/3 of the conventional hematite iron ores.^{1–5)} The ironsand consists of homogeneous particles in majority, and non-homogeneous particles. The homogeneous particle is composed of titanomagnetite (TTM), a magnetite (Fe₃O₄)–ilvospinel (Fe₂TiO₄) solid solution (Fe_{3–x}Ti_xO₄, with $x=0.27 \pm 0.02$). The non-homogeneous particle is composed of titanohematite (TTH, Fe_{2–y}Ti_yO₃) phase and TTM phase.^{4,6,7)}

The application of ironsand for the direct reduced iron (DRI) process has been studied for many decades. It has been known that the reduction of ironsand is slower than of hematite or magnetite iron ores.^{3,4,7–11)} In the reduction of ironsand by carbon monoxide, the complete reduction of iron oxides requires temperature above 1273 K with high reducing potential. In the previous work by the authors,⁷⁾ the reason for the stability of the ironsand against carbon monoxide atmosphere was suggested to be the structure and higher thermodynamic stability of TTM resulted from the existence of titanium.

While the mechanism of the reduction ironsand by carbon monoxide has been studied intensively by a few research groups,^{4,7–10)} the information on the reduction of ironsand by hydrogen is still not sufficient, especially in the kinetics and the phase transformation during the reduction. Because hydrogen is a major reducing agent in DRI

processes with carbon monoxide, it is necessary to clarify the mechanism of the reduction of ironsand by hydrogen for the future application.

This work presents results of reduction of ironsand by hydrogen, discusses the reduction mechanism by the examination of the phase transformation during the reduction, and compares with hematite and magnetite iron ores and previous data.

2. Experimental

The chemical compositions of ironsand and hematite iron ore examined in this work are presented in **Table 1**. The particle size of ores was screened to be in the range of 125–212 μm. The surface area was 1.2×10³ m²/kg for ironsand and 1.6×10³ m²/kg for hematite iron ore. The mass of the ore in each experiment was 2 g. The oxygen associated with iron was calculated to be 21.1 mass%. The extent of reduction was calculated as a mass fraction of oxygen in iron oxides removed in the course of reduction.

Reduction of ores using H₂–Ar gas mixture was studied in a laboratory fixed bed reactor in a vertical tube electric

Table 1. Chemical compositions (mass%) of ironsand and hematite iron ore.

Element	Fe _{tot}	Fe ²⁺	Fe ³⁺	TiO ₂	Al ₂ O ₃	MgO	SiO ₂	CaO	Mn
TTM ironsand	57.2	24.2	33.0	7.43	3.59	2.94	2.17	0.67	0.51
Hematite iron ore	62.7	-	62.7	0.08	2.61	-	4.81	-	0.04

Fig. 1. (a) Schematics of experimental set-up: 1 - reactor, 2 - pressure gauge, 3 - six way valve, 4 - rotameter, 5 - gas flow controller, 6 - gas purifier and 7 - heating tape. (b) Schematic experimental reactor.

furnace. Experimental set-up and the schematic of the reactor are presented in **Fig. 1**. After a sample was put into the reactor, it was purged with argon. Then the reactor was moved to the hot zone of the furnace. A sample was heated to a required temperature in argon atmosphere. Then the reducing gas mixture was introduced to the reactor. After certain reaction time, the reactor was pulled off from the hot zone of the furnace and quenched. The hydrogen and the argon used in the experiments were super high purity and high purity, respectively. The gases were purified before mixing by passing through traps filled with Drierite and 4 A molecular sieve to remove moisture. The composition of reducing gas was achieved using gas flow controllers (Brooks, Model 5850E). The outlet gas was analyzed on-line by a dew point sensor (General Eastern Hygro M4/D-2). The outlet gas line from the top of the reactor to the dew point sensor was heated by a heating-tape with temperature about 393 K. The total gas flow rate was maintained at $1.33 \times 10^{-5} \text{ m}^3/\text{s}$.

Samples were analyzed with X-ray Diffractometer (XRD, SIEMENS D5000). The XRD has a monochromator and a copper $K\alpha$ X-ray source. The voltage and current in the X-ray emission tube were set at 30 kV and 30 mA, respectively. The scanning rate on samples was set at $0.6^\circ/\text{min}$ with a step of 0.03° . The morphology of samples was observed by Field Emission Scanning Electron Microscope (FESEM, HITACHI S-4500). The extent of reduction was calculated as a mass fraction of oxygen in iron oxides removed in the course of reduction.

3. Results

3.1. Effects of Temperature

Reduction of ironsand by hydrogen was studied using H_2 -Ar gas mixtures in the temperature range of 973 to 1373 K. Reduction curves are presented in **Fig. 2**. In the experimental range, iron oxides in the ironsand were reduced to metallic iron completely at temperatures above

Fig. 2. Reduction of ironsand by 25vol% H_2 -Ar gas mixture at different temperatures.

1123 K. The degrees of reduction of the sample reduced at 973 and 1073 K after 2-h reduction were about 70 and 95%. The reduction rate increased with temperature from 973 to 1273 K; further increase in temperature to 1373 K had a negligible effect. At 1273 and 1373 K, the reduction extent increased linearly with time up to 80% of reduction and slowed down afterwards until the completion of the reduction. In the temperature range of 973 to 1173 K, the slope of the reduction curves slowly and steadily decreased, with increasing extent of reduction.

3.2. Effect of Hydrogen Content

Effect of hydrogen content on the reduction of ironsand was studied by reaction of ironsand with H_2 -Ar gas mixture at 1173 K. The hydrogen content was varied from 5 to 50 vol%. The reduction curves are presented in **Fig. 3**.

As shown in **Fig. 3**, increase in hydrogen content from 5 to 10 vol% caused a sharp increase in the reduction rate. Reduction rate increased with increasing hydrogen content up to 25 vol% H_2 ; further increase to 50 vol% had a relatively slight effect.

3.3. Phase Transformation during the Reduction of Ironsand by H₂-Ar Gas Mixture

Samples in the progress of reduction at 1173 K by 25vol%H₂-Ar gas mixture were analysed by XRD as shown in Fig. 4. Metallic iron was observed after 3 min of reduction, when the reduction extent was about 15%. Wüstite peaks were not detected except a trace in the XRD pattern of a sample reduced for 5 min. After 20 min, when the reduction extent achieved 80%, the peak for metallic

Fig. 3. Reduction of ironsand by H₂-Ar gas mixture with different H₂ content at 1173 K.

iron became dominant in the XRD pattern, and some traces of TTM peaks appeared. The reduction of TTM to wüstite proceeded much slower than reduction of wüstite to metallic iron. Wüstite was reduced very rapidly, what explains the weakness of wüstite peaks in the XRD patterns, which consistent with the results of the reduction by carbon monoxide by the authors.⁷⁾ In the XRD pattern of a sample reduced for 60 min, when 100% of reduction of iron oxides was achieved, the peaks of Ti-containing phases; TTM, ilmenite and Ti oxides, were not detected.

Figure 5 presents XRD patterns of the samples reacted by 25vol%H₂-Ar for 2 h at different temperatures from 973 to 1373 K. Due the high intensity of the iron peak at around 45°, a part of the whole pattern from 25 to 40° was enlarged for the identification of minor phases. While there is no evidence of Ti-containing phases in the XRD patterns of the sample reduced at 1173 K, those reduced at 973 and 1073 K contained Fe-Ti oxides (TTM and ilmenite) and the samples reduced at 1273 and 1373 K contained Ti oxide phase.

3.4. Morphology Changes during the Reduction of Ironsand by H₂-Ar Gas Mixture

Figures 6(a) to 6(d) present SEM images of samples reduced for 60 min at different temperatures, from 1073 to 1373 K. A sample reduced at temperature of 1073 K (Fig.

Fig. 4. XRD patterns of samples reduced by 25vol%H₂-Ar gas mixture at 1173 K, in the progress of reduction.

6(a)), exhibited iron whiskers forming the feather-like structure. It is because the low chemical reaction rate at the temperature. As reduction temperature increased, the whisker disappeared, resulting in the fine structure of metallic iron, with slight effects of sintering with temperature.

The change in morphology of particles of ironsand during the reduction by 25vol% H_2 -Ar gas mixture at 1 173 K was presented in Figs. 7(a) to 7(c) and Figs. 8(a) to 8(d). As discussed in the author's former work,⁷⁾ the homogeneous (TTM) and the non-homogeneous (TTM-TTH) particles showed different changes in morphology during reduction.

The reduction of the homogeneous TTM particles started in a topochemical way with the formation of reduced/unreduced interface (Fig. 7(a)). However, with the increase in the reduction time, the interface between reduced and unreduced zone in a particle became undistinguishable due to high diffusivity of hydrogen through pores (Fig. 7(b)). In a particle reduced for 60 min, when 100% reduction of iron oxides was achieved, the metallic iron phase had a fine structure (Fig. 7(c)).

In the reduction of non-homogeneous ironsand particles, metallic iron nucleated in the vicinity of TTH phase in the beginning of the reduction. The reduction of TTH to metal-

Fig. 5. XRD patterns of samples reduced by 25vol% H_2 -Ar gas mixture at different temperatures, after 2 h reaction.

Fig. 6. Morphology of samples reduced by 25vol% H_2 -Ar gas mixtures at different temperatures. (After 60 min reduction.)

Fig. 7. Morphology change of homogeneous TTM particles during the reduction by 25vol% H_2 -Ar gas mixture at 1 173 K.

Fig. 8. Morphology change of non-homogeneous particles during the reduction by 25vol% H_2 -Ar gas mixture at 1 173 K.

lic iron produced the needle-shape structure (Fig. 8(a)). The reduction of TTM started after TTH reduction (Fig. 8(b)). In a TTM grain, metallic iron grew to the core of the grain. Most of the non-homogeneous particles were completely reduced after 15 min of the reduction (Fig. 8(c)). After 60 min reduction, in spite of the effect of sintering on the structure of metallic iron, the initial phase boundary between TTM and TTH was distinguishable (Fig. 8(d)). Such a fast reduction of non-homogeneous particles containing TTH phase has been observed in the reduction by carbon monoxide,^{7,8)} and it is mainly because of the structural transformation during the reduction of TTH to TTM which opens the particle structure, resulting in acceleration of nucleation and growth of metallic iron, and facilitates further reduction of TTM phase.

4. Discussion

4.1. Mechanism of the Reduction of Ironsand by Hydrogen

In equilibrium state, the reduction of TTM in the Fe-Ti-O system proceeds the following path^{4,12,13)}:

The reduction path includes the formation of intermediate phases, ilmenite ($FeTiO_3$), $\text{ferrous-pseudobrookite}$ ($FeTi_2O_5$) and $\text{ferrous-pseudobrookite}$ ($FeTi_2O_5$). The standard Gibbs free energies for the reduction of ilmenite and $\text{ferrous-pseudobrookite}$ by hydrogen are as followings^{12,14)} (The data for $\text{ferrous-pseudobrookite}$ was not available):

Fig. 9. Equilibrium phase diagram according to partial pressure ratio of hydrogen to water in the experimental temperature range.

The equilibrium phase diagram according to the H_2 to H_2O ratio for the reactions (2) and (3) is presented in Fig. 9. In the experimental condition, 25vol% H_2 -Ar at 973 to 1 373 K, the complete reduction of iron oxides in ironsand can be achieved.

In the experimental range, the reduction temperature affected the composition of the final sample at each temperature as well as the extent of reduction, significantly. Table 2 presents the final reduction products at different temperature after 2-h reaction. Complete reduction of iron oxides in ironsand was achieved at temperatures above 1 123 K (Fig. 2). The sample reduced at 973 K contained iron and TTM phase, and the formation of ilmenite was detected in the sample reduced at 1 073 K. The XRD pattern of the sample reduced at 1 173 K only showed metallic iron peak while the samples reduced at higher temperatures presented the peaks of TiO_2 . It seems that TiO_2 in the sample reduced at 1 173 K was in an amorphous form, however, further investigation such as TEM observation is necessary for the clarification.

Table 2. Phases in samples reduced by 25vol% H_2 -Ar at different temperatures, after 2-h reaction. (Based on XRD analysis, Fig. 5.)

Temperature, K	Phases identified by XRD
973	Fe, TTM
1073	Fe, TTM, ilmenite ($FeTiO_3$)
1173	Fe
1273	Fe, TiO_2
1373	Fe, TiO_2

According to the XRD analysis (Fig. 4), the reduction path of TTM ironsand under the experimental condition is presented as follows:

The reduction path (4) observed did not contain the intermediate phases in the equilibrium reduction path (1). This phenomenon might be explained in kinetics during the phase transformation. In equilibrium state, the transformation in structure of Ti-containing phase during the reduction of ironsand can be presented by the following sequence:

The first step includes the transformation of TTM to ülvspinel with the rearrangements of Fe^{2+} in tetrahedral sites and octahedral sites in the lattice as shown in Eq. (6), and the further transformations combine a structural transformation.

(The structure of TTM at experimental temperature range was presented by the Akimoto model; *tetra*: tetrahedral site, and *octa*: octahedral site)¹⁵⁻¹⁸⁾

In experiments, XRD results (Fig. 4) showed that the slowest step in the reduction was TTM to wüstite. And the wüstite was reduced to metallic iron quite quickly. The fast reduction of wüstite has been discussed in the author's previous work.⁷⁾ The reduction of TTM starts with the reduction of Fe^{3+} to Fe^{2+} , accompanied by the removal of oxygen. Titanium in TTM stabilizes the spinel structure, and the slowest step in the reduction was the reduction of Fe^{3+} with the release of Fe^{2+} from the TTM phase ($TTM \rightarrow 'FeO' + \text{ülvospinel}$). For the equilibrium (sequences (1), (5) and (6)), the transformation of structure should take place without the contact between H_2 (or H_{ads}) and Fe^{2+} . However, it seemed that the high diffusivity of hydrogen did not allow Fe^{2+} ions to settle down onto the equilibrium position, resulting in the reduction path (4). When the reduction of iron oxides to metallic iron finished, the sintering

Fig. 10. Reduction of raw and preoxidized ironsand in comparison with hematite and magnetite iron ores, by 25vol% H_2 -Ar gas mixture at 1173 K. (POX: Preoxidized ironsand.)

effects with the increase in temperature and reaction time resulted in the growth of Ti oxide phase as shown in Fig. 5.

4.2. Effects of Preoxidation of Ironsand on the Reduction by Hydrogen

The effects of preoxidation of ironsand was examined in reduction of the preoxidized ironsand in comparison with hematite and magnetite iron ores at 1173 K using 25vol% H_2 -Ar gas mixture. The magnetite iron ore was achieved by partial reduction of the hematite iron ore by 7vol% CO -63vol% CO_2 -30vol%Ar at 1373 K for 4 h, and the preoxidized ironsand was obtained by heating ironsand at 1373 K for 72 h in air. The reduction curves of the minerals were presented in Fig. 10.

The preoxidation of ironsand increased the reduction rate, however, the both ironsand were reduced slower than the magnetite and the hematite iron ores which do not contain titanium. In the reduction of ironsand by carbon monoxide at 1373 K studied by the authors (Ref. 8)), preoxidized ironsand was reduced faster than magnetite iron ore, and the reduction rate was close to that of hematite iron ore because the structural transformation of rhombohedral (TTH) to spinel cubic (TTM) facilitate the further reaction.^{8,19,20)} However, in the reduction of ironsand by hydrogen, such a structural transformation did not affect much on the reduction rate. The main reason for the low reduction rate of ironsand compared with those of iron ores is thought to be the chemical stability of TTM in ironsand.

4.3. Comparison with Previous Studies

In this study, the reduction of ironsand by hydrogen was investigated. In the past, McAdam *et al.*¹⁰⁾ investigated the reduction of ironsand pellet which made of the New Zealand ironsand (same mineral examined in this paper), by 100% of hydrogen at 1173 K, and Morozov *et al.*¹¹⁾ studied the reduction of the preoxidized ironsand from Itrup Island (9.85 wt% TiO_2 , 57.43 wt% Fe_2O_3 , 22.15 wt% FeO and 3.25 wt% MgO) by 100% of hydrogen at 1173 K. The reduction of ironsand by hydrogen at 1173 K studied in this work was compared with the results of the previous works in Fig. 11. For the further comparison, the reduction curves of ironsand by 70vol% CO -Ar gas mixture at 1273 and 1373 K in the same experimental setup by the author⁷⁾ were also

Fig. 11. Reduction of raw and preoxidized ironsand in comparison with previous works. [Ref. 10): 100% H₂ at 1 173 K; Ref. 11): 100% H₂ at 1 173 K; and Ref. 7): Reduction of raw ironsand by 70%CO–Ar gas mixture. POX: preoxidized ironsand.]

presented.

The reduction curves of McAdams *et al.*'s work¹⁰⁾ showed a similar pattern to the present work. The preoxidation increased the reduction rate in both case. The reduction of the preoxidized ironsand from Itrup Island was quite slower than that of the New Zealand ironsand. It is thought that the high content of TiO₂ in the mineral might decrease the reduction rate.

In the reduction of ironsand by carbon monoxide, the reduction curves showed a parabolic period in the initial state of reduction. The rate of the reduction by hydrogen was higher than that by carbon monoxide, especially in the beginning of the reduction chiefly due to the high reduction potential and high diffusivity of hydrogen.^{20–23)} The reduction rate at 1 173 K by 25vol% H₂–Ar gas mixture was comparable to the rate at 1 373 K by 70vol% CO–Ar gas mixture.

5. Conclusion

The reduction of ironsand by hydrogen was examined in isothermal experiments, H₂–Ar gas mixtures in the temperature range of 973 to 1 373 K. The reduction mechanism was examined by morphology observation and XRD phase analysis.

With 25vol% H₂–Ar gas mixture, the complete reduction of iron oxides in ironsand was achieved at temperatures above 1 123 K. At 1 173 K, the reduction rate increased with hydrogen content in the reducing gas up to 25 vol% H₂,

however, the effect of the further increase in hydrogen content was negligible. During the reduction, ironsand was reduced to iron and iron-titanium oxides or titanium oxides, depending on the reduction temperature. At temperature above 1 173 K, the formation of the intermediate phases such as ilvospinel and ilmenite was not observed. The reduction path at temperatures above 1 173 K is suggested as follows:

Preoxidation of ironsand improved the reduction rate; however, the degree of the improvement was not as high as found in the reduction by carbon monoxide. The reduction rate in the reduction by hydrogen at 1 173 K was comparable to the rate by carbon monoxide at 1 373 K.

REFERENCES

- 1) A. Ohno and H. U. Ross: *Can. Metall. Q.*, **2** (1963), 259.
- 2) T. Marshall: *New Zealand J. Sci.*, **13** (1970), 3.
- 3) G. B. Sadykhov, L. O. Naumova and V. A. Rezinchenko: *Russ. Metall.*, (1992), 15.
- 4) G. D. McAdam: *Ironmaking Steelmaking*, **1** (1974), 138.
- 5) Market Price Data, April 2002, POSCO, Pohang, South Korea, (2002).
- 6) J. B. Wright: *New Zealand J. Geol. Geophys.*, **7** (1964), 424.
- 7) E. Park and O. Ostrovski: *ISIJ Int.*, **43** (2003), 1316.
- 8) E. Park and O. Ostrovski: *ISIJ Int.*, **44** (2004), 74.
- 9) E. Park, S. B. Lee, O. Ostrovski, D. J. Min and C. H. Rhee: *ISIJ Int.*, **44** (2004), 214.
- 10) G. D. McAdam, R. E. A. Dall and T. Marshall: *New Zealand J. Sci.*, **12** (1969), 649.
- 11) A. A. Morozov, V. A. Reznichenko, A. Y. Sinadskii and I. A. Karyazin: *Russ. Metall.*, (1998), 1.
- 12) S. Itoh, O. Inoue and T. Azakami: *Mater. Trans. JIM*, **39** (1998), 391.
- 13) A. F. Buddington and D. H. Lindsley: *J. Petrol.*, **5** (1964), 310.
- 14) E. T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, New York, (1980), 5.
- 15) S. Akimoto: *J. Geomag. Geoelect.*, **6** (1954), 1.
- 16) L. Neel: *Adv. Phys.*, **4** (1955), 191.
- 17) W. O'Reilly and S. K. Banerjee: *Phys. Lett.*, **17** (1965), 237.
- 18) R. Chevallier, J. Bolfa and S. Mathieu: *Bull. Soc. Franc. Min. Crist.*, **78** (1955), 307.
- 19) J. O. Edstrom: *J. Iron Steel Inst.*, **175** (1953), 289.
- 20) A. D. Pelton and C. W. Bale: *Direct Reduced Iron, Technology and Economics of Production and Use*, ed. by J. Feinman and D. R. MacRae, ISS, Warrendale, PA, (1999), 25.
- 21) A. A. El-Geassy, K. A. Shehata and S. Y. Ezz: *Trans. Iron Steel Inst. Jpn.*, **17** (1977), 629.
- 22) A. A. El-Geassy and V. Rajakumar: *Trans. Iron Steel Inst. Jpn.*, **25** (1985), 449.
- 23) I. J. Moon, C. H. Rhee and D. J. Min: *Steel Res.*, **69** (1998), 302.