Reduction of Titania–Ferrous Ore by Hydrogen

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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 1 373 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 1 123 K. At 1 173 K, the reduction rate increased with hydrogen content in the reducing gas up to 25vol%H₂. The composition of samples after 2-h reduction by 25vol%H₂–Ar depended on the reduction temperature. Below 1 073 K, the final sample contained iron and iron–titanium oxides. At temperatures above 1 173 K, the final sample was composed of iron and titanium oxide. The reduction path at temperatures above 1 173 K is suggested as follows:

Fe₃₋ₓTiₓO₄→FeOₓ+Feₓ₋₀₂₋ₓTiₓ₋₀₂₋ₓO₄→Fe+xFeO+yTiO₂ (0<δ<1−x)

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

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe₂O₃</th>
<th>FeO⁺</th>
<th>FeO⁻</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTM ore</td>
<td>19.9</td>
<td>33.6</td>
<td>6.7</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Hematite ore</td>
<td>62.7</td>
<td>62.7</td>
<td>0.08</td>
<td>2.64</td>
<td>4.81</td>
<td>0.64</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 online 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 1.33×10⁻³ m³/s.

Samples were analyzed with X-ray Diffractometer (XRD, SIEMENS D5000). The XRD has a monochromator and a copper Kα 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°/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 iron sand by hydrogen was studied using H₂–Ar gas mixtures in the temperature range of 973 to 1 123 K. The degrees of reduction of the sample reduced at 973 and 1 073 K after 2-h reduction were about 70 and 95 %. The reduction rate increased with temperature from 973 to 1 273 K; further increase in temperature to 1 373 K had a negligible effect. At 1 273 and 1 373 K, the reduction extent increased linearly with time up 80 % of reduction and slowed down afterwards until the completion of the reduction. In the temperature range of 973 to 1 173 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 iron sand was studied by reaction of iron sand with H₂–Ar gas mixture at 1 173 K. The hydrogen content was varied from 5 to 50 vol%. 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% H₂; 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 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. 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. 3).
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 iron sand during the reduction by 25 vol% H$_2$–Ar gas mixture at 1173 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 iron sand particles, metallic iron nucleated in the vicinity of TTH phase in the beginning of the reduction. The reduction of TTH to metal-

![Image](https://example.com/image1)

**Fig. 5.** XRD patterns of samples reduced by 25 vol% H$_2$–Ar gas mixture at different temperatures, after 2 h reaction.

![Image](https://example.com/image2)

**Fig. 6.** Morphology of samples reduced by 25 vol% H$_2$–Ar gas mixtures at different temperatures. (After 60 min reduction.)

![Image](https://example.com/image3)

**Fig. 7.** Morphology change of homogeneous TTM particles during the reduction by 25 vol% H$_2$–Ar gas mixture at 1173 K.

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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, 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:

\[
\begin{align*}
\text{Fe}_3\text{Ti}_2\text{O}_7 & \rightarrow \text{FeO} + \text{Fe}_2\text{TiO}_4 \\
\text{Fe}_2\text{TiO}_4 & \rightarrow \text{Fe} + \text{Fe}_2\text{TiO}_4 \\
\text{Fe}_2\text{TiO}_3 & \rightarrow \text{Fe} + \text{Fe}_2\text{TiO}_4 \\
\text{FeTi}_2\text{O}_5 & \rightarrow \text{Fe} + \text{TiO}_2 \\
\text{FeTiO}_3 & \rightarrow \text{Fe} + \text{H}_2\text{O} \\
\text{Fe}_3\text{Ti}_2\text{O}_7 + \text{H}_2 & \rightarrow \text{Fe} + \text{Fe}_2\text{TiO}_4 + \text{H}_2\text{O} \\
\Delta G^\circ (\text{J/mol}) & = 24116.4 - 7.497T \\
\text{FeTi}_2\text{O}_5 + \text{H}_2 & \rightarrow \text{Fe} + \text{TiO}_2 + \text{H}_2\text{O} \\
\Delta G^\circ (\text{J/mol}) & = 34916.4 - 7.077T 
\end{align*}
\]

The equilibrium phase diagram according to the \(\text{H}_2\) to \(\text{H}_2\text{O}\) ratio for the reactions (2) and (3) is presented in Fig. 9. In the experimental condition, 25vol\%\text{H}_2–\text{Ar} at 973 to 1373 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 1123 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 1073 K. The XRD pattern of the sample reduced at 1173 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 1173 K was in an amorphous form, however, further investigation such as TEM observation is necessary for the clarification.
According to the XRD analysis (Fig. 4), the reduction path of TTM iron sand under the experimental condition is presented as follows:

\[
\begin{align*}
\text{Fe}_3\text{Ti}_4\text{O}_9 & \rightarrow \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Ti}^{4+} + \text{O}^2- \\
& \rightarrow \text{Fe} + \text{Fe}_{1-x}\text{Ti}_x\text{O}_4
\end{align*}
\]

(‘FeO’ is non-stoichiometric iron oxide, \(0 < \delta < 1 - x\))

\(\text{........................................(4)}\)

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 iron sand can be presented by the following sequence:

TTM (spinel cubic) → ilüvospinel (spinel cubic)

→ ilmenite (rhombohedral)

→ ferrous-pseudobrookite (orthorhombic) → rutile .......(5)

The first step includes the transformation of TTM to ilüvospinel 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.

\[
\begin{align*}
\text{Fe}_{1-x}^{2+}\text{Fe}^{3+}\text{Fe}^{2+}_{3}\text{Ti}^{4+}_{4}\text{O}_{9} & \rightarrow \text{Fe}^{2+}, \text{Ti}^{4+}\text{O}_4
\end{align*}
\]

(\(\text{........................................(6)}\))

The structure of TTM at experimental temperature range was presented by the Akimoto model; \(\text{tetra: tetrahedral site, and octa: octahedral site}\).\(^{15-18}\)

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 → FeO\(^{+}\) + ilüvospinel). For the equilibrium (sequences (1), (5) and (6)), the transformation of structure should take place without the contact between \(\text{H}_2\) (or \(\text{H}_2\text{O}\)) and Fe\(^{2+}\). However, it seems 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 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 iron sand was examined in reduction of the preoxidized iron sand in comparison with hematite and magnetite iron ores at 1 173 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 1 373 K for 4 h, and the preoxidized iron sand was obtained by heating iron sand at 1 373 K for 72 h in air. The reduction curves of the minerals were presented in Fig. 10.

The preoxidation of iron sand increased the reduction rate, however, the both iron sands were reduced slower than the magnetite and the hematite iron ores which do not contain titanium. In the reduction of iron sand by carbon monoxide at 1 373 K studied by the authors (Ref. 8)), preoxidized iron sand 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) facilitates the further reaction.\(^{8,15,20}\) However, in the reduction of iron sand by hydrogen, such a structural transformation did not affect much on the reduction rate. The main reason for the low reduction rate of iron sand compared with those of iron ores is thought to be the chemical stability of TTM in iron sand.

4.3. Comparison with Previous Studies

In this study, the reduction of iron sand by hydrogen was investigated. In the past, McAdam et al.\(^{10}\) investigated the reduction of iron sand pellet which made of the New Zealand iron sand (same mineral examined in this paper), by 100% of hydrogen at 1 173 K, and Morozov et al.\(^{11}\) studied the reduction of the preoxidized iron sand from Itrup Island (9.85 wt% TiO\(_2\), 57.43 wt% Fe\(_2\)O\(_3\), 22.15 wt% FeO and 3.25% MgO) by 100% of hydrogen at 1 173 K. The reduction of iron sand by hydrogen at 1 173 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 iron sand by 70vol%CO–Ar gas mixture at 1 273 and 1 373 K in the same experimental setup by the author\(^7\) were also

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**Table 2.** Phases in samples reduced by 25vol\%H\(_2\)–Ar at different temperatures, after 2-h reaction. (Based on XRD analysis, Fig. 5.)

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Phases identified by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
<td>Fe, TTM</td>
</tr>
<tr>
<td>1073</td>
<td>Fe, TTM, ilmenite (FeTiO(_3))</td>
</tr>
<tr>
<td>1173</td>
<td>Fe</td>
</tr>
<tr>
<td>1273</td>
<td>Fe, TiO(_2)</td>
</tr>
<tr>
<td>1373</td>
<td>Fe, TiO(_2)</td>
</tr>
</tbody>
</table>

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**Fig. 10.** Reduction of raw and preoxidized iron sand in comparison with hematite and magnetite iron ores, by 25vol%H\(_2\)–Ar gas mixture at 1 173 K. (POX: Preoxidized iron sand.)
The reduction of iron oxides in ironsand was achieved at temperatures above 1,123 K. At 1,173 K, the reduction rate increased with the 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, iron oxides were 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 ulvospinel and ilmenite was not observed. The reduction path at temperatures above 1,173 K is suggested as follows:

\[
\begin{align*}
\text{Fe}_3\text{Ti}_x\text{O}_y & \rightarrow \text{FeO'} + \text{Fe}_{3-x}\text{Ti}_x\text{O}_4 \\
& \rightarrow \text{Fe} + \text{Fe}_{3-x}\text{Ti}_x\text{O}_4 \rightarrow \text{Fe} + x\text{TiO}_2, \\
(0 < \delta < 1 - x)
\end{align*}
\]

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