Simultaneous Synthesis of Iron Carbide and Rutile from Ilmenite Ore by Thermochemical Reactions

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Simultaneous synthesis of iron carbides (mainly Fe3C) and rutile (TiO2) from natural ilmenite ore (mainly FeTiO3) were examined by thermochemical reactions with H2–CO or H2–CH4 gas mixtures at temperatures of 1 073–1 273 K. The low sulfur pressures incapable of forming FeS was added to these gas mixtures to make stable iron carbides without free carbon. Iron carbide is currently interesting as alternative pure iron sources in steelmaking. The rutile is also available as a feedstock for titanium industry.

First, partial conversion from ilmenite to rutile and metallic iron mostly proceeded and subsequently iron carbidization occurred together with further reduction of rutile. Finally, these processes with both gas mixtures provided iron carbide (Fe3C) and lower titanium oxides such as Magneli phases (Ti_nO_2-n, 4≤n≤9 namely TiO2–1/2) and/or Ti3O5 rather than rutile.

Reaction time, H2/CH4 ratio, sulfur potential, and temperature dependence of reaction behavior was examined further. The iron carbidization rates were analysed using the first order rate model. Ilmenite samples prepared from reagents showed slightly slower conversion rates to titanium oxides at 1 073 K than the natural ore ones, though both samples showed similar iron carbidization rates.

KEY WORDS: ilmenite ore; reagent ilmenite; simultaneous synthesis of iron carbide and rutile; thermochemical reactions; H2–CO or H2–CH4 gas mixtures; sulfur potential.

1. Introduction

The titanium industry consists of paint pigments and metallic products. As their main feedstocks, natural rutile (TiO2) and ilmenite ore (FeTiO3) are known. In the future it is supposed that the latter has a potential to be useful as the main resource because the former is diminishing.

As an example, the Becher process is operated commercially, in which ilmenite ore is partially reduced with reductants such as coal in a rotary kiln and subsequently an aqueous oxygen leaching is performed with NH4Cl solution to remove ferrous components and produce synthetic rutile.1) However this process remains a troublesome problem to treat the ferrous wastes.2) So that, another process will be proposed in this study to explore further possibility to process or upgrade ilmenite ore without any waste problems.

In the present work, we have tried to produce both iron carbides and rutile (TiO2) from ilmenite ore by utilizing pyrometallurgical reactions between solids and reducing gas, imaging that both products could be subsequently separated by any means.

Iron carbide is currently focused as an alternative iron source to steel scrap.3–5) If this process is operated successfully, it could supply both valuable titanium and ferrous materials simultaneously into each industry and generate benefits from wastes. As for iron carbide, we have reported several papers in which it was proved that traces of sulfur in reaction gas makes iron carbides more stable without any soot precipitation from many types of iron ores.6–9)

2. Experimental

Natural ilmenite ore (Ore I, ilmenite deposited in Quilon, Kerala, India. Main mineral: FeTiO3) was employed for reaction tests. The chemical composition is given in Table 1. Also, according to a reference,10) synthetic ilmenite (reagent I) was prepared from mixing some reagents of pure metallic iron, Fe2O3 and rutile (TiO2) with the stoichiometric proportion (FeTiO3), compacting to disks and heating at 1 473 K under argon gas in order to elucidate influence of gangue species on reaction behavior.

| Table 1. Chemical composition of ilmenite ore (mass%). |
|-------------|-------------|-------------|-------------|-------------|-------------|
| TiO2 | FeO | Fe2O3 | Al2O3 | SiO2 | CaO |
| 60.5 | 9.85 | 24.88 | 1.00 | 1.40 | 0.15 |
| MgO | MnO2 | Cr2O3 | V2O5 | P2O5 | ZrO2 |
| 0.65 | 0.40 | 0.14 | 0.28 | 0.17 | 0.60 |
The natural or the synthetic ilmenite was crushed and screened between 0.15–0.21 mm diameter to further subject to reaction tests.

A batch of ilmenite particles of 0.8 g weighed in a porcelain boat was reacted with H₂–CO or H₂–CH₄ mixtures under atmospheric pressure in a silica reactor (22 mm inner diameter) heated isothermally at 1 073–1 273 K by an electric furnace with SiC elements. The flow rate and the composition of gas mixtures were in the range of H₂/CO or H₂/CH₄ (cm³/min)/(cm³/min)). Using a H₂–0.2vol%H₂S gas cylinder, traces of gaseous sulfur H₂S was added into these gases in the proportion of \(\frac{P_{H_2S}}{P_{H_2}}\) = \(6.3 \times 10^{-5}\)–\(4.8 \times 10^{-3}\), which are also represented as the sulfur activity in inlet gas, \(a_s\). The value \(a_s\) is defined on the basis of partial gas pressure ratio \(\frac{P_{H_2S}}{P_{H_2}}\) at Fe/FeS equilibrium \(^6\)\(^7\) as listed in Table 2 (Eq. (1)).

\[
a_s = \left(\frac{P_{H_2S}}{P_{H_2}}\right) / \left(\frac{P_{H_2S}}{P_{H_2}}\right)_e
\]

The reason to provide sulfur activity in inlet gas is because traces of gaseous sulfur is effective to form iron carbides stably as proved in our previous researches \(^6\)–\(^9\). This is derived from that sulfur has a strong property chemisorbed on the surfaces of reduced iron and iron carbide. And then, the Goto method \(^1\)\(^1\) enabling to evaluate thermal equilibrium states of chemical reactions confirmed that the calculated values \(a_s\) nearly equal to inlet ones under given experimental conditions.

Based on our previous experimental conditions suitable for producing iron carbides with iron ore A (San Ishidro) in a ceramic boat by H₂–CO or H₂–CH₄ gas mixtures under atmospheric pressure \(^6\)\(^7\), the present experimental conditions of \(a_s\) and temperature were selected to produce iron carbides with lower levels of sulfur.

X-ray powder diffraction patterns were obtained for specimens cooled after reaction in a similar manner employed previously \(^6\)–\(^9\). The existing solid phases were identified referring to ASTM cards, and their contents, including inert gangues, were determined quantitatively by using the intensities of each independent diffraction peak (Table 3), empirical calibrations derived from each standard material prepared from chemical reagents, and chemical analysis. Standard samples of TiO₂, Ti₃O₇, and Ti₄O₉ were prepared by sealing samples in evacuated silica tubes and heating them \(^1\)\(^2\)–\(^1\)\(^3\). Total carbon and sulfur contents in the sample were determined by means of infrared oxygen combustion.

### 3. Experimental Results

X-ray diffraction patterns of the specimen after reaction identified the existence of phases Fe₃C (\(\theta\) phase), and free carbon (graphitic soot) as well as metallic Fe, and moreover ilmenite, TiO₂ (rutile), Ti₃O₇ and Ti₄O₉ by referring to ASTM cards. These are shown typically in Figs. 1(a)–1(d). Each content of products was calculated by using mass bal-

<table>
<thead>
<tr>
<th>Materials</th>
<th>Fe</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>Fe₃O₄</th>
<th>θ-Fe₃C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (degree)</td>
<td>82.33</td>
<td>41.93</td>
<td>35.45</td>
<td>33.15</td>
<td>37.74</td>
</tr>
<tr>
<td>FeTiO₃</td>
<td>211</td>
<td>200</td>
<td>311</td>
<td>104</td>
<td>210</td>
</tr>
<tr>
<td>TiO₂ (Rutile)</td>
<td>596</td>
<td>596</td>
<td>596</td>
<td>596</td>
<td>596</td>
</tr>
<tr>
<td>Ti₃O₇</td>
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<td>596</td>
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</tr>
<tr>
<td>Ti₄O₉</td>
<td>596</td>
<td>596</td>
<td>596</td>
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<td>596</td>
</tr>
</tbody>
</table>

### Table 3. Position of independent peaks (2θ(degree), X-ray: Cu Kα1)

<table>
<thead>
<tr>
<th>C</th>
<th>Fe</th>
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<td>210</td>
</tr>
<tr>
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<td>596</td>
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<td>596</td>
<td>596</td>
<td>596</td>
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<td>596</td>
</tr>
</tbody>
</table>

Fig. 1. Typical X-ray diffraction patterns after reactions of ilmenite ore.
(a) \(H_2/CO=200/200\), \(a_s=0.1\), 1 073 K, 10 min, (b) \(H_2/CO=200/200\), \(a_s=0.1\), 1 073 K, 60 min, (c) \(H_2/CH_4=200/200\), \(a_s=0.05\), 1 173 K, 60 min, (d) \(H_2/CH_4=200/200\), \(a_s=0.1\), 1 273 K, 60 min.
ances among Ti, iron, and inert gangue before and after re-
action, calibration from standard samples and chemical
analysis of total carbon. The Ti oxides not identified by X-
ray diffraction could be anticipated Magneli phases
(Ti$_{n}$O$_{2n-1}$, $4 \leq n \leq 9$, namely TiO$_{2-1}$). Therefore, we des-
ignated these products Ti$_{O_2}$ phases. In this work, only
Ti$_4$O$_7$ not Ti$_5$O$_9$ was identified as one of Magneli phases.
Also, in this work, iron oxides (Fe$_2$O$_3$, Fe$_3$O$_4$, FeO) and
iron carbide Fe$_x$C ($\chi$ phase, nonstoichiometry $x=2.0–2.6$)9)
did not almost appear.

### 3.1. Time Dependency

**Figure 2** shows the time dependency on product contents
obtained for the conditions: H$_2$/CO=200/200, $P_{H_2}/P_{CO}=2.1 \times 10^{-4}$, $a_0=0.10$, and 1 073 K for ore I. First, ilmenite is
partially reduced to metallic iron and rutile, according to
Eq. (2) as shown in Fig. 1(a). Then rutile is further reduced
to Ti$_{O_2}$ according to Eq. (3). Afterward iron carbidiza-
tion began at 20 min according to Eqs. (4), (5) and (6) and
considerable iron carbide Fe$_x$C ($\theta$ phase) was formed at
60 min as shown in Fig. 1(b). For 120 min, the fractional
iron carbidization (defined later as Eq. (8)) was as large as
0.93 with 3.9 mass% free carbon and Ti oxides including a
little Ti$_3$O$_5$. The largest half of Ti oxides was occupied by
Ti$_{O_2}$ phases.

\[
\text{FeTiO}_3 + H_2 = Fe + TiO_2 + H_2O \quad \text{(2)}
\]
\[
\text{nTiO}_2 + H_2 = Ti_{O_2} + H_2O \quad \text{(3)}
\]
\[
2CO = C + CO_2 \quad \text{(4)}
\]
\[
H_2 + CO = C + H_2O \quad \text{(5)}
\]
\[
3Fe + C = Fe_3C \quad \text{(6)}
\]

**Figure 3** shows the time dependency on product contents
obtained for the conditions: H$_2$/CH$_4=200/200$, $P_{H_2}/P_{CH_4}=1.95 \times 10^{-4}$, $a_0=0.05$, and 1 173 K for ore I. During the first
period the reactions proceeded similarly to Fig. 2. Beyond
30 min, iron carbidization began to proceed according to
Eqs. (6) and (7) and simultaneously ilmenite was almost reduced to Ti$_n$O$_{2n-1}$ phases, where Ti$_4$O$_7$ phase appeared clearly (Fig. 1(c)) and the content increased gradually with time. Finally at 90 min the fractional iron carbidization was as large as 0.56 with 4.5 mass% free carbon, 11.5 mass% metallic iron and Ti oxides.

3.2. Temperature Dependency

Figure 4 shows the variation of product contents at different reaction temperatures for the conditions of H$_2$/CO=200/200, $a_r=0.10$ and 60 min reaction for ore I. It was found that the content of $\theta$ phase decreases with increasing temperatures and that rutile appears at temperatures less than 1 173 K and both Ti$_2$O$_3$ and Ti$_4$O$_7$ phases appear at 1 273 K while remaining Ti oxides are Ti$_n$O$_{2n-1}$ phases.

Figure 5 shows the variation of product contents at different temperatures for the conditions of H$_2$/CH$_4$=200/200, $a_r=0.05$ and 60 min reaction for ore I. It was found that the content of $\theta$ phase has a maximum at 1 223 K and that Ti$_4$O$_7$ phase appears at temperatures greater than 1 173 K and Ti$_4$O$_3$ phase appears as half as contents of Ti oxides with much free carbon at 1 273 K (Fig. 1(d)). Until 1 223 K, amounts of Ti$_2$O$_3$ phase increased with increasing temperatures.

Comparing Fig. 4 with Fig. 5, a reverse temperature tendency to promote iron carbidization for H$_2$–CO and H$_2$–CH$_4$ mixtures can be recognized. With the former gas mixture, iron carbide predominates at lower temperatures.

As for microstructures, microscopic dispersion of small particles having nearly $5 \mu$m diameter in porous Ti oxides was observed as shown in Fig. 6, which was taken for a cross section obtained for the reaction condition of 1 273 K and 60 min in Fig. 4 (fractional iron carbidization $f_q=0.12$). These small particles were supposed to consist of metallic iron and iron carbides by EPMA. Zhao et al. reacted a disk made of smaller particles of synthesized ilmenite (less than $45 \mu$m) with CO gas and observed a little different microstructures from this work. In their samples, individual ilmenite particles mainly comprised of porous iron, porous rutile, and unreacted ilmenite layers topochemically.

3.3. Sulfur Activity Dependency

Figure 7 shows dependency of sulfur activity in gas on
product contents obtained for the conditions of $\text{H}_2/\text{CO}=200/200$, $a_s=0.05$–0.40, and 60 min reaction at 1 073 K for ore I. Above $a_s=0.05$ it was found that the content of $\theta$ phase amounted to a constant around 20 mass% without free carbon, while much soot appeared with less $\theta$ phase at $a_s=0$. As for Ti oxides, nearly 20 mass% rutile and much Ti$_x$O$_{2n-1}$ phases were produced independently of sulfur activity except $a_s=0$. Appreciable Ti$_3$O$_5$ phase appeared only at $a_s=0$.

Figure 8 shows dependency of sulfur activity in gas on product contents obtained for the conditions of $\text{H}_2/\text{CH}_4=200/200$, $a_s=0.05$–0.40, and 60 min reaction at 1 173 K for ore I. It was found that the content of $\theta$ phase decreases with increasing sulfur activity $a_s$ from 0.05 until 0.40, while much free carbon precipitated with $\theta$ phase at $a_s=0$. Ti$_3$O$_5$ phase had a minor content tendency to increase with decreasing sulfur activity, though Ti$_x$O$_{2n-1}$ phases mostly existed.

### 3.4. Gas Composition $\text{H}_2/\text{CH}_4$ Dependency

Figure 9 shows the variation of product contents with gas composition $\text{H}_2/\text{CH}_4$ for ore I, $a_s=0.05$, 60 min at
173 K. It was found that the content of $\theta$ phase decrease with decreasing the flow rate of CH$_4$ and Ti$_4$O$_{2n-1}$ phases are mostly produced with considerable amounts of Ti$_4$O$_7$ phase a little dependently on the gas composition.

3.5. Conversion from Ilmenite to Ti Oxides and Iron Carbides

Conversion from ilmenite to Ti oxides and iron carbides are defined as follows, respectively.

The fractional conversion from ilmenite to Ti oxides $f_{\text{Ti Oxides}}$ can be roughly defined as Eq. (8).

$$f_{\text{Ti Oxides}} = \frac{\sum \text{ Ti oxide (mol%)}}{\text{Total Ti (mol%)}} \ldots (8)$$

The fractional iron carbidization $f_{\theta}$ can be defined as Eq. (9).

$$f_{\theta} = \frac{3\text{Fe}_3\text{C (mol%)}}{\text{Total Fe (mol%)}} \ldots \ldots \ldots (9)$$

Figures 10 and 11 show both fractional conversion $f_{\text{Ti oxides}}$ and $f_{\theta}$ for four kinds of test conditions. For ore I at all temperatures it was found that the conversion from ilmenite to Ti oxides and metallic iron proceeds mostly in the first stage and then iron carbidization begins around the phase when the first stage finalizes mostly.

The second stage seems to proceed more favorably at a lower temperature such as 1 073 K, because it gives a high value $f_{\theta}$=0.92 at 120 min, while at the same temperature, the conversion to Ti oxides is almost finalized at the short time until 40 min.

On the other hand, ilmenite samples prepared from reagents showed fairly slower conversion rates to titanium oxides at 1 073 K than ilmenite ores, probably because of containing no gangues available as promoter for reduction, while showing that both specimens provide similar iron carbidization rates.

4. Discussion

4.1. Reduction Reaction

In this work, several Ti oxides of rutile (TiO$_2$), Ti$_4$O$_n$, Ti$_3$O$_8$, and not both anatase (TiO$_2$) and Ti$_5$O$_9$ were identified as products by X-ray diffraction.

On the other hand, Zhang et al.\textsuperscript{16} had reacted TiO$_2$ with H$_2$–CH$_4$ gas mixture at 1 573 K and identified Ti$_5$O$_9$ as one of products. These different observations from ours are probably attributed to their reactions at higher temperatures such as 1 573 K.
4.2. Iron Carbidization Reaction

In our previous study concerning production of iron carbide from iron ore, we have reported that iron carbidization proceeds according to the first order rate model.8,9) Therefore, this model was applied to the iron carbidization process during reaction of ilmenite ore by using Eq. (10).

\[
df/dt = k(1-f_q)...........................(10)
\]

Here, \( k \) is the iron carbidization rate constant \((s^{-1})\) and \( t \) is reaction time \((s)\).

In this work the titanium carbidization did not occur because the present tests were carried out under the conditions remaining a plenty of Ti oxides at less than 1 273 K. Welham et al.14) had studied mechanically activated carbothermic reduction of ilmenite and reported the existence of TiC at temperatures greater than 1 373 K.

Figure 12 shows \( k \) values obtained for the reaction of ore I with H\(_2\)-CO mixtures including dependence of sulfur activity in gas on \( k \) values obtained for iron ore A reported previously.9) The value \( k \) for ore I was one third as large as iron ore A, probably due to less total iron content in ilmenite ore. Also, iron ore A had a maximum \( k \) value around \( a_s=0.05 \). These results seem to correspond to sulfur activity dependence of iron carbide contents as shown in Fig. 7. Iron carbidization behavior of ilmenite ore was almost the same as that for iron ore depending on sulfur activity and temperature. Namely, favorable conditions to produce iron carbide without soot by reacting ilmenite ore with two types of gaseous sulfur bearing gas mixtures corresponded well to both temperature conditions of 1 073 K for H\(_2\)-CO and 1 173 K for H\(_2\)-CH\(_4\) mixtures as shown in Figs. 4 and 5. These both conditions were in a good agreement with ours obtained earlier in iron ores.5,7) Therefore, coexisting Ti oxides seem to behave as inert species for iron carbidization of ilmenite ore.

4.3. Further Researches

The rutile (TiO\(_2\)) is available for the manufacture of paint and pigments in titanium industry. Iron carbide is currently the preferred alternative to pure iron sources in steelmaking. Therefore, both these products need to be separated further by such means as magnetic force after crushing them or leaching them with a solution. These will require more researches in the future.

5. Conclusion

Simultaneous synthesis of iron carbides (mainly cementite Fe\(_3\)C, \( \theta \) phase) and rutile (TiO\(_2\)) from natural ilmenite ore (mainly FeTiO\(_3\)) were investigated by thermochemical reactions with H\(_2\)-CO or H\(_2\)-CH\(_4\) gas mixtures having low sulfur pressures incapable of forming FeS at temperatures of 1 073–1 273 K.

For the ilmenite samples it was confirmed that traces of sulfur in both gas mixtures produce iron carbides stably without free carbon, analogous to our previous results obtained for iron ores.

In the first stage, partial conversion from ilmenite to rutile and metallic iron proceeded and then iron carbidization occurred with further reduction of rutile. Both gas mixtures provided iron carbide and lower titanium oxides such as Magneli phases (Ti\(_n\)O\(_{2n-1}\), \( 4\leq n\leq9 \), namely TiO\(_2\)) and/or TiO\(_2\) rather than rutile during the later stages.

The content of \( \theta \) phase decreased with decreasing the flow rate of CH\(_4\) in H\(_2\)-CH\(_4\) gas mixtures.

TiO\(_2\) and Ti\(_4\)O\(_7\) phases tended to exist with increasing temperatures rather than TiO\(_2\). Only TiO\(_2\) was identified as one of the Magneli phases.

Ilmenite reagents showed slightly slower conversion rates to titanium oxides than ilmenite ores at 1 073 K, probably
due to the absence of gangues, though both ilmenites provided similar iron carbidization rates.

The iron carbidization rates were analysed using the first order rate model. The iron carbidization rate constant for ilmenite ore was one third as large as that obtained previously for iron ore, probably due to less total iron content in ilmenite ore.

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