Selective Enrichment and Separation of Ti–Fe Enriched Mineral from Ti-bearing Electric Furnace Slag with Metallic Iron as Carrier

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(Received on March 31, 2017; accepted on June 5, 2017; J-STAGE Advance published date: August 4, 2017)

A new process of selective enrichment and separation of Ti-bearing minerals from the Ti-bearing electric furnace slag (TEFS) with metallic iron as carrier was proposed in this paper. The thermodynamic analysis, melting process and selective reduction were carried out, with an emphasis on the effects of Fe2O3/slag ratio and H2 partial pressure on the processes. The results indicated that the major Ti-bearing mineral in TEFS was pseudobrookite after adding Fe2O3 into the molten slag. In the selective reduction process, the pseudobrookite particle in the modified slag was selectively reduced to the magnetic Ti–Fe enriched mineral particle embedded with metallic iron. Then the magnetic Ti–Fe enriched mineral particle was separated from the nonmagnetic silicate particle in magnetic separation process. Finally, the Ti–Fe enriched mineral with 61.1 wt% TiO2 and 18.31 wt% Total Fe was obtained. Furthermore, the recovery ratio of TiO2 and Total Fe were 85% and 78.6%, respectively. The contents of CaO and SiO2 of the Ti–Fe enriched mineral were 1.4 wt% and 1.9 wt%, which were much less than that of TEFS. The Ti-bearing mineral in TEFS was effectively concentrated as using the new selective enrichment and separation method.

KEY WORDS: Ti-bearing slag; pseudobrookite; reduction; enrichment; metallic iron.

1. Introduction

China is rich in vanadium titanomagnetite resources. The amount of vanadium and titanium in Panzhihua-Xichang region of China accounts for 11.6 wt% and 35.17 wt% of world reserves, respectively.1) Currently, vanadium titanomagnetite ore is usually mineral separated into vanadium titanomagnetite concentrate, ilmenite concentrate and other minerals in Panzhihua-Xichang region. Vanadium titanomagnetite concentrate, containing about 52% titanium and 89% vanadium of the vanadium titanomagnetite ore, is commonly used to produce iron and extract vanadium using the conventional blast furnace process.2–4) However, the titanium resource remains in the Ti-bearing blast furnace slag (22–25 wt% TiO2) without effective utilization.5) Other methods6–12) developed or under development to utilize vanadium titanomagnetite concentrate are the direct reduction-electric furnace smelting process, the sodium salt roasting-direct reduction-electric furnace smelting process, the direct reduction-magnetic separation and so on. In addition, the direct reduction-electric furnace smelting process has been commercialized in South Africa and New Zealand, which has the advantages of large production scale and mature vanadium recovery technology.5) However, there is no effective method to recover titanium from TEFS for the utilization of vanadium titanomagnetite concentrate and the development of direct reduction-electric furnace smelting process.

There were many processes1,13) developed or under development all over the world to utilize the titanium resource in TEFS, including the preparation of nanostructured titanium dioxide, the hydrochloric acid leaching of TEFS for titanium dioxide preparation. However, these processes resulted in high costs, poor recovery or environmental pollutions due to the complex interfacial combination of Ti-bearing mineral and gangue in TEFS. In addition, the selective enrichment method was used to recover titanium resource from the Ti-bearing blast furnace slag in many studies with advantages such as large production scale, simple devices and environmental friendly.14,15)

In the selective enrichment process, the titanium in Ti-bearing slag was enriched into the target Ti-bearing mineral phase. The major target Ti-bearing minerals were perovskite, anosovite, rutile and TiC6N6.16) Wang et al.17) enriched titanium of the Ti-bearing blast furnace slag into perovskite, and separated the perovskite product containing 35–45 wt% TiO2 with the TiO2 recovery ratio at 38–42%. Lei et al.18) pointed out the Ti-bearing minerals in the slag could be transformed to anosovite by adding SiO2 up to 35 wt% under the C/CO equilibrated atmospheres. Wang et al.19) pointed out the 80–150 µm anosovite can be obtained by adding 3% P2O5 into the slag in the reducing atmosphere with the cooling rate of 17°C/min. Zhang et al.20) indicated the titanium in the slag could be oxidized...
to rutile with particle size of 24 μm under the conditions of melting at 1520°C for 30 min and cooling rate at 2°C/min. Xue et al.\(^{21}\) enriched the titanium into TiC_{x}N_{y} which was difficult to be recovered for its largest particle size of 30 μm was too small to be separated. Besides, it is well known that high CaO content is harmful to the sulfuric acid process and chlorination process. Therefore, according to current researches, it indicated that perovskite is difficult to be utilized by leaching methods due to its high CaO content. Moreover, the rutile and TiC_{x}N_{y} crystals are difficult to grow up, leading to the difficulty of milling and separation. In addition, there are not sharp physical or chemical properties distinctions between the target Ti-bearing minerals mentioned above and the gangue, which lead to the difficulty of separation and low recovery efficiency.

The key of selective enrichment method is the target Ti-bearing mineral that can be easy crystallized and has obvious physio-chemical distinctions with the gangue.\(^{14}\) Pseudobrookite was proposed as a new target Ti-bearing mineral phase in this paper based on three main reasons reported previously.\(^{22}\) Firstly, pseudobrookite was easier to grow up than rutile and TiC_{x}N_{y} crystals. Secondly the CaO content of pseudobrookite was less than that of perovskite. Thirdly, the iron in pseudobrookite could be selectively reduced to metallic iron embedded in the Ti-bearing mineral particle. Moreover, the magnetic Ti–Fe enriched mineral particle could be easily separated from other nonmagnetic gangues by magnetic separation which is simple and environmentally friendly.\(^{23}\) Furthermore, pseudobrookite could be obtained through the melting process as using the thermal energy of hot molten slag separated in the electric smelting process. In the reduction process of pseudobrookite, hydrogen was chosen as reductant due to its high reductive efficiency in the low temperature range.

In the present study, the thermodynamic analysis, fundamental study of the selective enrichment and the reduction of TEFS were investigated. The melting and selective reduction experiments were carried out, with an emphasis on the effects of Fe_{2}O_{3}/slag ratio and H\(_{2}\) partial pressure on the process. The findings would provide a new technical basis for the effective utilization of the titanium resource in TEFS.

2. Experimental

2.1. Material

The TEFS used in this study was produced in the direct reduction-electric furnace smelting process with the vanadium titanomagnetite concentrate in Panzhihua-Xichang region of China. The chemical composition of TEFS is listed in Table 1. It can be seen that the TiO\(_{2}\) content of TEFS is 47.35 wt%, and the major impurities are aluminum, silicon, magnesium. The XRD patterns of TEFS is shown in Fig. 1. The major mineral phases in TEFS are M\(_{x}\)Ti\(_{3−x}\)O\(_{5}\) (0≤x≤2, M=Ti, Fe, Mg, Al), diopside and spinel. The H\(_{2}\) was used as a reductant in this study. The gas purity of H\(_{2}\) and N\(_{2}\) were above 99.9%. Ferric oxide (Fe\(_{2}\)O\(_{3}\)) of analytical reagent (AR) grade was employed as an additive.

### Table 1. Chemical composition of the original TEFS (wt%).

<table>
<thead>
<tr>
<th>Component</th>
<th>TiO(_{2})</th>
<th>Total Fe</th>
<th>V(<em>{2})O(</em>{5})</th>
<th>Al(<em>{2})O(</em>{3})</th>
<th>SiO(_{2})</th>
<th>MgO</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>47.35</td>
<td>3.16</td>
<td>0.49</td>
<td>12.10</td>
<td>16.08</td>
<td>9.88</td>
<td>9.97</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of the original TEFS.

2.2. Experimental

2.2.1. Experimental Apparatus and Procedure

2.2.1.1. Melting

The experimental flowsheet is illustrated in Fig. 2. A certain amount of TEFS and Fe\(_{2}\)O\(_{3}\) powder were mixed well. The mixture was loaded in a 250 ml corundum crucible and heated at 1773 K for 30 min in an airtight high temperature furnace (furnace cavity \(\Phi\times 250 \times 250\) mm). After melting, the power supply to furnace was turned off and the furnace temperature was cooled to room temperature. The mixture was in N\(_{2}\) atmosphere with gas flow of 3 L/min over the melting and cooling processes. The modified slag was prepared for the analysis of mineral phases and microstructure. Based on those results, reduction process was discussed.

2.2.1.2. Reduction Roasting

Reduction roasting was performed in a silica tube of 50 mm in inside diameter which was hung in a vertical resistance furnace. The schematic diagram of the apparatus is shown in Fig. 3. The modified slag was crushed and ground to 74 μm. The fine modified slag was completely mixed with 1% starch and 10% distilled water to pelletize into green pellets of 10–14 mm in diameter. Those pellets were dried in an oven at 105°C for 4 h. 40 g dried pellets were loaded in the silica tube. Then N\(_{2}\) was charged into the reac-
tor at 4 L/min. After the system was appropriately purged by N2, the silica tube was slowly introduced into the high temperature zone of vertical resistance furnace at 10 cm/min. When the target temperature was reached, the H2−N2 gas mixture was introduced into the silica tube reactor. The total linear velocity of gas was 0.05 m/s at which the resistance of gas external diffusion could be neglected. After the reduction continued for 60 min, H2 was closed and N2 continued to purge the whole system. Finally, the silica tube was taken out from the furnace and cooled down to room temperature in N2 atmosphere. The reduced slag was prepared for analysis of mineral phases, microstructure, element distribution. Based on those results, magnetic separation was discussed.

2.2.1.3. Magnetic Separation
20 g cooled reduced pellets were crushed manually to 1 mm and ground in a ball mill with solid/liquid ratio of 1:1. The particle size was less than 45 μm. The slurry was separated by wet magnetic separation using a magnetic tube with the magnetic field intensity at 0.075 T. Then the obtained magnetic and nonmagnetic fractions were separately filtered by a water-circulation vacuum pump and dried in a vacuum drying oven. The magnetic and nonmagnetic fractions were prepared for analysis of chemical composition and mineral phase.

2.2.2. Definition of Parameters
The TiO2 (Total Fe) recovery ratio is calculated by Eq. (1).

\[ \varepsilon (\%) = \frac{\beta \times \gamma}{\alpha} \] ............................... (1)

where \( \varepsilon \ (\%) \) is the recovery ratio of TiO2 (or Total Fe), \( \alpha \) (wt%) is the TiO2 (or Total Fe) content of magnetic separation feedstock, \( \beta \) (wt%) is the TiO2 (or Total Fe) content of product (magnetic fraction or nonmagnetic fraction), and \( \gamma \) (%) is the yield of product (magnetic fraction or nonmagnetic fraction).

2.2.3. Analytical Methods
FactSage 7.0 (Thermfact/CRCT, Montreal, QC, Canada; GTT-Technologies, Herzogenrath, Germany) was used to analyze the thermodynamics.

The chemical compositions of the titanium slag and products were determined by X-ray fluoroscopy (XRF, Axios mAX, Holand PANalytical Co., Ltd).

The scanning electron microscope equipped with an energy diffraction spectrum analyzer (SEM-EDS, JEOL JSM-6490LV, Japan) was used to study the microstructure and element analysis of the slags.

The mineral phases of the samples were characterized by X-ray diffraction (Cu Kα radiation, \( \lambda = 0.154056 \) nm, 40 kV, 250 mA, SCAN: 10.0/80.0/0.02/.15 sec, D/max2550PC, Rigaku Co., Ltd., Japan).

3. Thermodynamic Analysis
3.1. The Formation of Modified Slag
3.1.1. Ti-bearing Solid Solution
The main Ti-bearing mineral in TEFS is \( M_xTi_{3-x}O_5 \) (0≤x≤2), in which the M represents Ti, Mg, Al, Fe and other elements. In order to transform \( M_xTi_{3-x}O_5 \) (0≤x≤2) to pseudobrookite, the slag must contain enough amount of iron oxide. The Total Fe of TEFS is only 3.16 wt%, therefore, iron oxide must be added into the molten slag.

When Fe2O3 is added into the molten slag, the new mineral phase in the Ti-bearing slag will be formed after the slag cooled and crystallized. The temperature of the molten slag is 1 773 K in the electric melting process, thus, the main reactions in the molten slag can be simply expressed as Eq. (2). The \( \Delta G \) was calculated by the Reaction Module of Factsage.

\[ Fe_2O_3 (s) + TiO_2 (s) = Fe_2TiO_5 (s) \]

\[ \Delta G^{\circ}_2 = -10.0 \text{ kJ/mol at 1773 K} \] ............................... (2)

The Equilib Module of Factsage was used to calculate the mineral species and contents of the modified slag with different addition amount of Fe2O3. Figure 4 shows the minerals contents of modified slag vs. the Fe2O3/Slag ratio with

![Fig. 3. Schematic diagram of the apparatus. 1-cylinder. 2-gas flowmeter. 3-mixer. 4-elevator. 5-Heating Elements. 6-pellets. 7-shaft furnace. 8-thermocouple. 9-silica tube. 10-gas outlet.](image)

![Fig. 4. The minerals contents of the modified slag vs. the addition amount of Fe2O3.](image)
the molten slag cooling from 1873 K to 173 K. According to the calculate results, the major mineral phases in modified slag are pseudobrookite (Fe$_2$TiO$_3$), spinel (MgAl$_2$O$_4$), silicate (CaAl$_2$Si$_2$O$_8$) and a small amount of perovskite (CaTiO$_3$). The contents of the pseudobrookite, silicate and perovskite decrease with increasing the Fe$_2$O$_3$/Slag ratio, while the spinel content increases as the Fe$_2$O$_3$ addition amount increases.

3.1.2. Si-Fe-bearing Solid Solution
Because a certain quality of SiO$_2$ exists in the slag, the iron oxide can combine with SiO$_2$ and CaO to form some complex compounds in the slag. In order to reveal the performance of iron oxide combine with SiO$_2$ and CaO, the ternary diagram SiO$_2$–CaO–FeO (Fig. 5) is studied in this part. The CaO/SiO$_2$ mass ratio of TEFS is 0.62. Thus, the main silicate mineral phase in the slag will change along the black double arrow according to the iron oxide amount added into molten slag. It is clear that a large proportion of iron oxide combined with Ti-bearing mineral is transformed to pseudobrookite as shown in Fig. 4, a small amount of iron oxide exists in the silicate. Therefore, the main mineral phase of the silicate may be pseudowollastonite (α - CaO·SiO$_2$) and wollastonite (β - (Ca, Fe)O·SiO$_2$). In addition, in the real molten slag, the other oxides in the slag, such as MgO, Al$_2$O$_3$ and TiO$_2$, can also exist in the silicate as complex solid solution, which makes the complex solid solution more stable.

According to the thermodynamic analysis of the modified slag, iron oxide exists in the modified slag is beneficial for the formations of the pseudobrookite and Si-Fe-bearing solid solution.

3.2. The Selective Reduction of Modified Slag
The thermodynamic analysis of modified slag shows that the main Fe-bearing minerals of modified slag are the pseudobrookite and Si-Fe-bearing solid solution. The Si-Fe-bearing solid solution can be considered as a mixture of FeSiO$_3$ and CaSiO$_3$, which makes calculation simple. In order to achieve the selective reduction of pseudobrookite, it is necessary to analyze the reduction thermodynamics of pseudobrookite and FeSiO$_3$.

The Ti-bearing mineral can be separated from gangues by magnetic separation unless the iron in pseudobrookite is reduced to metallic iron. In the pseudobrookite reduction process, iron ions are reduced as Fe$^{3+}$→Fe$^{2+}$→Fe$^0$ process. The reduction process of Ti-bearing mineral is Fe$_2$TiO$_3$ → Fe$_2$TiO$_4$ → FeTiO$_3$ → FeTiO$_5$ → TiO$_2$, which can be expressed as follow:

\[
\text{Fe}_2\text{TiO}_3(s) + \text{H}_2(g) = \text{Fe}_2\text{TiO}_4(s) + \text{H}_2\text{O}(g) \quad \ldots (3) \\
\Delta G^\circ = -26869.6 - 37.6T \text{ J/mol} \\
\text{Fe}_2\text{TiO}_4(s) + \text{H}_2(g) = \text{FeTiO}_3(s) + \text{Fe}(s) + \text{H}_2\text{O}(g) \quad \ldots (4) \\
\Delta G^\circ = 35238.5 - 13.4T \text{ J/mol} \\
2\text{FeTiO}_3(s) + \text{H}_2(g) = \text{FeTiO}_5(s) + \text{Fe}(s) + \text{H}_2\text{O}(g) \quad \ldots (5) \\
\Delta G^\circ = 32754.9 - 15.3T \text{ J/mol} \\
\text{FeTi}_2\text{O}_5(s) + \text{H}_2(g) = 2\text{FeTiO}_3(s) + \text{Fe}(s) + \text{H}_2\text{O}(g) \quad \ldots (6) \\
\Delta G^\circ = 12840.9 + 6.6T \text{ J/mol}
\]

The FeSiO$_3$ is reduced by hydrogen can be expressed as:

\[
\text{FeSiO}_3(s) + \text{H}_2(g) = \text{SiO}_2(s) + \text{Fe}(s) + \text{H}_2\text{O}(g) \quad \ldots (7) \\
\Delta G^\circ = 76380.3 - 39.3T \text{ J/mol}
\]

The ΔG$_r$, which determines the occurrence of reaction in standard state, relates to ΔG°, reaction temperature and H$_2$ partial pressure. The relationship of ΔG$_r$, ΔG°, T and p is shown in Eq. (8).

\[
\Delta G_r = \Delta G^\circ + RT\Sigma\ln p^v \ldots (8)
\]

where, ΔG$_r$ is the change of gibbs free energy in the reaction, J/mol; ΔG° is the change of gibbs free energy in standard state, J/mol; R is molar gas constant, 8.314 J/(mol·K); T is the reaction temperature, K; p is the gas partial pressure, Pa; v is the stoichiometric coefficient of gas in the reaction.

When the ΔG$_r$ is zero, the reaction can process towards right spontaneously. The plot of H$_2$ partial pressure vs. reaction temperature as ΔG$_r$ equals to zero is shown in Fig. 6, in

![Fig. 5. The ternary diagram of SiO$_2$–CaO–FeO (mass ratio).](image-url)
which the total pressure of H₂ and N₂ gas mixture is 1 atm. The plots are the required minimum \( p(\text{H}_2) \) when the reactions process towards right. In the temperature range from 800 K to 1 300 K, the \( p(\text{H}_2) \) of Eq. (7) is much higher than that of Eqs. (3) to (6). It indicates that a higher H₂ partial pressure is required to reduce FeSiO₃ to Fe and SiO₂. The reduction process of Fe₂TiO₅ occurred in the order of Eqs. (3) to (6). Metallic iron begins to be generated when Eq. (4) proceed. Therefore, in order to achieve reducing pseudobrookite to metallic iron, the appropriate H₂ partial pressure is in the area between lines of Eqs. (7) and (4), as shown in the shadow area of Fig. 6.

4. Results and Discussion

4.1. Effect of Fe₂O₃/Slag Ratio on the Modified Slag Microstructure

The 100 g TEFS and different mass of Fe₂O₃ were mixed well and melted at 1 773 K for 30 min in N₂ atmosphere. Figure 4 shows that the slope of pseudobrookite changes remarkably at the Fe₂O₃/Slag ratio of 0.17, which means the titanium more rapidly reacts with impurity to form gangue mineral after the Fe₂O₃/Slag ratio is above 0.17. In this work, four Fe₂O₃/Slag ratio of 0.1, 0.17, 0.3 and 0.4 are chosen to study the effect of Fe₂O₃/Slag ratio on the modified slag SEM microstructure, as shown in Fig. 7. The EDS analysis of the modified slags is listed in Table 2. As shown in Fig. 7(a), the white pseudobrookite particles embed in the gangue phases of silicate and spinel. The size of gangue mineral embed between the pseudobrookite particles is too small to separate from pseudobrookite, even though the columnar pseudobrookite particle has a large particle size. When the Fe₂O₃/Slag ratio is 0.17, as shown in Fig. 7(b), the pseudobrookite and gangue particles become much larger than that of Fe₂O₃/Slag ratio at 0.1 and the boundary is clear. The Fe is mainly distributed in the pseudobrookite particles. The major elements in spinel are Al and Mg. As the Fe₂O₃/Slag ratio increase from 0.17 to 0.3, the shapes of pseudobrookite particles change from columnar to plate-like and many small Fe-bearing spinel particles embed in the silicate, as shown in Fig. 7(c). The Fe content of spinel reaches 42 wt%, which is easily reduced to metallic iron in the follow reduction process, in addition, too much metallic iron in the gangue is adverse to the magnetic separation. Figure 7(d) indicates many cross-shaped iron oxide crystals appear as the Fe₂O₃/Slag ratio reaches 0.4, which indicates the Fe₂O₃ is much excess in the modification process. By comparing the microstructures and Fe distributions of the modified slags, the embedment relationship between pseudobrookite and gangue is simple as the Fe₂O₃/Slag ratio is 0.17, which is more beneficial to the pseudobrookite particles liberated in milling than that of other modified slags. In addition, the Fe in the modified slag with Fe₂O₃/Slag ratio of 0.17 mainly distributes in the pseudobrookite instead of spinel, which is more beneficial to the selective reduction of pseudobrookite than that of other modified slags.

The XRD of the modified slag with Fe₂O₃/Slag ratio of 0.17 is shown in Fig. 8. It is obvious that the main mineral

Table 2. EDS analysis of mineral phases in different modified slags (wt%).

<table>
<thead>
<tr>
<th>NO.</th>
<th>Position</th>
<th>Ti</th>
<th>Fe</th>
<th>Ca</th>
<th>Si</th>
<th>Mg</th>
<th>Al</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fig. 7(a)</td>
<td>63.81</td>
<td>10.92</td>
<td>/</td>
<td>/</td>
<td>2.22</td>
<td>2.70</td>
<td>20.35</td>
</tr>
<tr>
<td>2</td>
<td>Fig. 7(a)</td>
<td>3.71</td>
<td>0.44</td>
<td>/</td>
<td>/</td>
<td>15.99</td>
<td>36.17</td>
<td>43.69</td>
</tr>
<tr>
<td>3</td>
<td>Fig. 7(a)</td>
<td>3.80</td>
<td>0.39</td>
<td>11.03</td>
<td>23.38</td>
<td>9.62</td>
<td>6.08</td>
<td>45.70</td>
</tr>
<tr>
<td>4</td>
<td>Fig. 7(b)</td>
<td>55.89</td>
<td>15.72</td>
<td>/</td>
<td>/</td>
<td>2.84</td>
<td>3.10</td>
<td>22.45</td>
</tr>
<tr>
<td>5</td>
<td>Fig. 7(b)</td>
<td>1.43</td>
<td>3.84</td>
<td>/</td>
<td>/</td>
<td>15.39</td>
<td>35.11</td>
<td>44.23</td>
</tr>
<tr>
<td>6</td>
<td>Fig. 7(b)</td>
<td>8.78</td>
<td>3.99</td>
<td>11.48</td>
<td>19.85</td>
<td>22.45</td>
<td>22.45</td>
<td>22.45</td>
</tr>
<tr>
<td>7</td>
<td>Fig. 7(c)</td>
<td>42.42</td>
<td>21.88</td>
<td>/</td>
<td>/</td>
<td>2.95</td>
<td>3.61</td>
<td>29.15</td>
</tr>
<tr>
<td>8</td>
<td>Fig. 7(c)</td>
<td>0.71</td>
<td>42.00</td>
<td>/</td>
<td>/</td>
<td>7.06</td>
<td>14.32</td>
<td>35.91</td>
</tr>
<tr>
<td>9</td>
<td>Fig. 7(c)</td>
<td>9.01</td>
<td>14.32</td>
<td>14.23</td>
<td>16.57</td>
<td>2.65</td>
<td>5.74</td>
<td>37.49</td>
</tr>
<tr>
<td>10</td>
<td>Fig. 7(d)</td>
<td>36.46</td>
<td>28.64</td>
<td>/</td>
<td>/</td>
<td>2.78</td>
<td>3.11</td>
<td>29.01</td>
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<tr>
<td>11</td>
<td>Fig. 7(d)</td>
<td>/</td>
<td>65.10</td>
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<td>/</td>
<td>1.66</td>
<td>2.24</td>
<td>31.00</td>
</tr>
<tr>
<td>12</td>
<td>Fig. 7(d)</td>
<td>7.07</td>
<td>14.32</td>
<td>14.29</td>
<td>18.20</td>
<td>3.17</td>
<td>5.12</td>
<td>37.84</td>
</tr>
</tbody>
</table>

Fig. 7. The SEM microstructures of the different modified slags (a: Fe₂O₃/Slag ratio = 0.1, b: Fe₂O₃/Slag ratio = 0.17, c: Fe₂O₃/Slag ratio = 0.3, d: Fe₂O₃/Slag ratio = 0.4).

Fig. 8. XRD patterns of the modified slag and different reduced slag.
phases of the modified slag are pseudobrookite, diopside and spinel. The XRD of the modified slag is consistent with the thermodynamic and SEM-EDS analysis of the modified slag. This result effectively supports for the reduction roasting and magnetic separation in the follow-up process.

4.2. Effect of H\textsubscript{2} Partial Pressure on the Reduced Slag

The H\textsubscript{2} partial pressure difference between Eqs. (4) and (7) is maximum when the reaction temperature is 1 123 K, as indicated in Fig. 6. Thus 1 123 K is chosen as the reaction temperature to study the effects of H\textsubscript{2} partial pressure on the reduction. The modified slag is reduced by H\textsubscript{2}−N\textsubscript{2} gas mixture. The total pressure of H\textsubscript{2}−N\textsubscript{2} gas mixture remains at 1 atm. In this work, three H\textsubscript{2} partial pressure of 0.8 atm (Point A), 0.9 atm (Point B) and 1.0 atm (Point C) are chosen to study the effect of H\textsubscript{2} partial pressure on the reduced slag, as shown in Fig. 6. The XRD of the modified slag and the different reduced slags, as shown in Fig. 8, indicates that the diffraction peaks of pseudobrookite gradually weaken with increasing the H\textsubscript{2} partial pressure. When the H\textsubscript{2} partial pressure is 0.8 atm, the ulvospinel phase is detected in the modified slag. It means that the pseudobrookite is reduced to ulvospinel as follows.

\[
\text{Fe}_2\text{TiO}_4(s) + \text{H}_2(g) = \text{Fe}_2\text{TiO}_4(s) + \text{H}_2\text{O}(g) \ldots \ldots (9)
\]

The metallic iron and ilmenite phases are detected as the H\textsubscript{2} partial pressure reaches 0.9 atm, which indicates the Fe\textsubscript{2}TiO\textsubscript{4} has been reduced to Fe and FeTiO\textsubscript{3} as follows.

\[
\text{Fe}_2\text{TiO}_4(s) + \text{H}_2(g) = \text{FeTiO}_3(s) + \text{Fe}(s) + \text{H}_2\text{O}(g) \ldots \ldots (10)
\]

The diffraction peaks of metallic iron and ilmenite weakens as the H\textsubscript{2} partial pressure increases from 0.9 to 1 atm. The XRD of the different reduced slags indicates the reduction process is in accord with the reduction thermodynamic analysis of the modified slag.

4.3. Effect of H\textsubscript{2} Partial Pressure on the Magnetic Separation

In this work, three H\textsubscript{2} partial pressure of 0.8 atm, 0.9 atm and 1.0 atm were chosen to study the effect of H\textsubscript{2} partial pressure on the magnetic separation. The effect of H\textsubscript{2} partial pressure on the magnetic separation is listed in Table 4. When the H\textsubscript{2} partial pressure is 0.8 atm, the yield of magnetic fraction is only 5.2% because most of the Fe in pseudobrookite are not reduced to metallic iron, as shown in Fig. 8. When the H\textsubscript{2} partial pressure is 0.9 atm, the yield and TiO\textsubscript{2} content of magnetic fraction are 60.1% and 61.1 wt%, respectively, which is consistent with the results of Fig. 9. When the H\textsubscript{2} partial pressure reaches 1 atm, the TiO\textsubscript{2} content of magnetic fraction is only 54.2 wt%. Because the FeSiO\textsubscript{3} in gangue is reduced to metallic iron at 1 123 K, as shown in Eq. (7) and Fig. 6, which is magnetic and easily mixed with the magnetic Ti–Fe enriched fraction in the magnetic separation.

4.4. Properties of the Products

Table 5 and Fig. 10 are the chemical composition and XRD patterns of the products shown in Table 4 as H\textsubscript{2} partial pressure is 0.9 atm. The Ti–Fe enriched mineral contains 61.1 wt% TiO\textsubscript{2} and 18.31 wt% Total Fe. The SiO\textsubscript{2} and CaO contents of the Ti–Fe enriched mineral are 1.9 wt% and 1.4

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### Table 3. EDS analysis of mineral phases in reduced slag (wt%).

<table>
<thead>
<tr>
<th>Point</th>
<th>Ti</th>
<th>Fe</th>
<th>Si</th>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>—</td>
<td>100</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>62.42</td>
<td>11.66</td>
<td>—</td>
<td>—</td>
<td>3.42</td>
<td>4.84</td>
</tr>
<tr>
<td>3</td>
<td>11.58</td>
<td>5.8</td>
<td>21.98</td>
<td>13.72</td>
<td>12.01</td>
<td>19.1</td>
</tr>
</tbody>
</table>

---

### Table 4. The effect of H\textsubscript{2} partial pressure on the magnetic separation.

<table>
<thead>
<tr>
<th>H\textsubscript{2} partial pressure/atm</th>
<th>products</th>
<th>Yield/%</th>
<th>TiO\textsubscript{2}/Content wt%</th>
<th>Total Fe</th>
<th>TiO\textsubscript{2}</th>
<th>Total Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8 Magnetic fraction</td>
<td>5.2</td>
<td>63.1</td>
<td>19.2</td>
<td>7.6</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>Nonmagnetic fraction</td>
<td>44.8</td>
<td>42.0</td>
<td>13.7</td>
<td>92.4</td>
<td>92.9</td>
<td></td>
</tr>
<tr>
<td>0.9 Magnetic fraction</td>
<td>60.1</td>
<td>61.1</td>
<td>18.31</td>
<td>85.0</td>
<td>78.6</td>
<td></td>
</tr>
<tr>
<td>Nonmagnetic fraction</td>
<td>39.9</td>
<td>16.5</td>
<td>7.74</td>
<td>15.0</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td>1 Magnetic fraction</td>
<td>71.3</td>
<td>54.2</td>
<td>16.7</td>
<td>89.8</td>
<td>85.1</td>
<td></td>
</tr>
<tr>
<td>Nonmagnetic fraction</td>
<td>28.7</td>
<td>15.2</td>
<td>7.26</td>
<td>10.2</td>
<td>14.9</td>
<td></td>
</tr>
</tbody>
</table>

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### Table 5. Chemical composition of the products (wt%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO\textsubscript{2}</th>
<th>Total Fe</th>
<th>V\textsubscript{2}O\textsubscript{5}</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>SiO\textsubscript{2}</th>
<th>MgO</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic fraction</td>
<td>61.10</td>
<td>18.31</td>
<td>0.38</td>
<td>8.10</td>
<td>1.90</td>
<td>6.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Nonmagnetic fraction</td>
<td>16.50</td>
<td>7.74</td>
<td>0.49</td>
<td>15.40</td>
<td>29.40</td>
<td>9.60</td>
<td>19.30</td>
</tr>
</tbody>
</table>
and magnetic separated from TEFS.

Based on the thermodynamic analysis and the magnetism was investigated as adding a certain amount of Fe$_2$O$_3$. The Ti-bearing mineral was selectively enriched from TEFS with metallic iron as carrier and the gangue can be used as the ingredient of cement and cast stone.

5. Conclusions

The fundamental study on the enrichment of Ti–Fe enriched mineral from TEFS with metallic iron as carrier was investigated as adding a certain amount of Fe$_2$O$_3$. The CaO and SiO$_2$ content of the Ti–Fe enriched mineral were 1.4 wt% and 1.9 wt%, respectively, which were much less than that of TEFS.

(3) Ti–Fe enriched mineral with 61.1 wt% TiO$_2$ and 18.31 wt% Total Fe was obtained. The recovery ratios of TiO$_2$ and Total Fe were 85% and 78.6%, respectively. The Ti–Fe enriched mineral can be the high quality synthetic rutile product can be the feedstock for sulfuric acid leaching process. When the impurities in the Ti–Fe enriched mineral are removed by further treatment, the Ti-bearing product can be the high quality synthetic rutile and the gangue grains.

REFERENCES