New Separation Method of Boron and Iron from Ludwigite Based on Carbon Bearing Pellet Reduction and Melting Technology

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Ludwigite is the most abundant boron resource in China. In order to fully utilize the complex ore and meet the boron and iron consumption of the country, a new process was proposed in this research. Fine ludwigite and pulverized coal were pelletized and then reduced isothermally at high temperatures. The influence of reduction conditions, such as reduction temperature and C/O (mole ratio), on the metallization degree and melting morphology of the samples, were studied in detail. The pellet could not melt well at higher or lower temperature than 1 673 K. The increase in C/O could improve the reduction and melting rate of the pellet. The appropriate temperature and C/O were 1 673 K and 1.2 in the work. When the pellet was reduced at 1 673 K for 12 min, the iron and slag separated in a clean manner. The apparent activation energy of reduction stage was 180.17 kJ/mol. The boron content of nugget and boron oxide (B₂O₃) content of the slag were 0.065% and 20.01%, respectively. In addition, the microstructure, phase transformation and phases composition of the samples were characterized by means of XRD, SEM, EDS and optical microscope. The efficiency of extraction of boron (EEB) of the slag was 86.46% when it was cooled in a slow method. The boron-bearing nugget and boron-rich slag were good raw materials for steelmaking and borax production.

KEY WORDS: ludwigite; boron and iron separation; reduction and melting; iron nugget; boron-rich slag.

1. Introduction

Traditional boron resource-szaibelyite ore of China is going to running out and it becomes more and more difficult to meet the increasing need for boron products of the country. Ludwigite deposit in Liaoning and Jilin province, which accounts for 57.88% boron reserves in China, is the main alternate resource of szaibelyite ore. The average chemical composition of the ore is (wt%): TFe30.65%, B₂O₃7.23% and MgO24.59%. It is a kind of complex ore of iron, boron and magnesium, but the valuable elements of boron and iron can’t be directly extracted from the ore by traditional methods because of their low grades.1)

In the exploring the appropriate method to utilize the ludwigite, the key problems are the separation degree of boron and iron and their qualities for further production. Many Chinese researchers have devoted themselves to the comprehensive utilization of the complex iron ore.2–5) Due to the complicated mineralogy and very fine mineral dissemination, it is difficult to get single boron concentrate and iron concentrate through magnetic separation or magnetic separation combined with flotation and selective reduction. Although the hydrometallurgical method can separate boron and iron perfectly, the excessive acid consumption causes very high cost, equipment erosion and environmental pollution. In order to efficiently separate boron and iron from the complex ore, some researchers put forward pyrometallurgical routes, i.e. ‘blast furnace’ and ‘solid reduction-electric arc furnace melting’ methods.6) The BF method not only consumes a lot of expensive coke and has a long production flow chart, but the B₂O₃ will also badly erode the lining refractory. The second one can’t find out an appropriate method for the solid direct reduction of the iron ore and it will also consume a lot of precious power resources. Both the two methods face the same problem that the efficiency of extraction of boron (EEB) of the separation slag is low. It will affect the yield of boron resource. So, the resource of ludwigite hasn’t been put into the practical industrial production at present.

In order to efficiently utilize ludwigite ore and overcome the current existing problems (i.e. coke or electricity assumption, refractory erosion, low EEB of the slag and so on), a new pyrometallurgical process has been proposed by the author’s laboratory for the boron and iron separation based on coal bearing pellet reduction and melting technology, which is a kind of low CO₂ emission, fast, low investment cost and environmental-friendly ironmaking technology.7–11) The aims of this work are to investigate the isothermal reduction and melting behavior of the composite pellets at high temperatures and the properties of the separation products.

2. Experimental

2.1. Raw Materials

The ludwigite ore used in this study is obtained from Dandong, in Liaoning Province of China. The chemical composition of the complex ore sample is shown in Table

<table>
<thead>
<tr>
<th>Component</th>
<th>Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>30.65%</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>7.23%</td>
</tr>
<tr>
<td>MgO</td>
<td>24.59%</td>
</tr>
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</table>

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After ball-milling, the particle size of the ludwigite is shown in Table 2. The mineralogical analysis of the ludwigite is investigated by XRD. The result in Fig. 1 indicates that the main crystalline phases are magnetite (Fe\textsubscript{3}O\textsubscript{4}), szaboelyte (Mg\textsubscript{2}(OH)[B\textsubscript{2}O\textsubscript{4}(OH)]) and chrysotile (Mg\textsubscript{3}[Si\textsubscript{2}O\textsubscript{5}](OH)\textsubscript{4}). The pulverized anthracite coal is used as a reductant, which is screened by 1 mm opening sieve after ball-milling. The chemical composition of the coal is listed in Table 3, which shows that the coal is high in fixed carbon, and comparatively low in ash, volatile, sulfur and phosphorus. It is a good reducing agent for carbon-bearing direct reduction.

The reactivity of the pulverized coal is assessed by chemical reaction ability between pulverized coal and carbon dioxide (30 mL/min) by thermogravimetric method with a heating speed of 10 K/min. The result is shown in Fig. 2. Other chemicals used in this research are of analytical reagent (AR) grade.

### 2.2. Experimental Procedure

In the experiments, the ludwigite and pulverized coal were mixed with a mole ratio of fixed carbon to reducible oxygen of 1.0, 1.2 and 1.4. Furthermore, one kind of organic binder of 2 wt% of the mixture was added and the moisture of the mixture was controlled as 7 wt%. At last, all the materials were completely mixed by rigorously stirring for about 30 min. The prepared mixture was pelletized in a horizontal twin rollers machine. The size of the pillow shape pellet was 40×30×20 mm.

Reduction and melting process was performed in a closed MoSi\textsubscript{2} muffle resistance furnace, in which the temperature was controlled to within ±3 K. In each experiment, the dry green composite pellets were put into a graphite crucible and then heated at the temperatures ranging from 1 573 to 1 723 K in the furnace. The crucible had already been heated to the target temperature before the reduction beginning. In addition, purge gases were not utilized and experiments were run at atmospheric conditions. Once the reduction experiments finished, the samples were taken out of the furnace and cooled to ambient temperature under the protection of nitrogen.

The pellets, which didn’t melt and became into metallized pellets, were tested by the index of metallization degree (ε). The ε was calculated by the following formula:

\[
\eta = \left( \frac{M_{Fe}}{T_{Fe}} \right) \times 100\% \quad \text{........................................... (1)}
\]

where \(T_{Fe}\) is the content of total iron after reduction, \(M_{Fe}\) is the content of metallic iron after reduction. Both of them were analyzed by chemical method.

In order to evaluate the efficiency of extraction of boron (EEB) of the boron-rich slag, the normal pressure alkaline leaching method was applied. The parameters of the method was described as follows: Amount of boron-rich slag: 4.000 g, Particle size of slag: <0.074 mm, Concentration of lye: 20 wt% NaOH, V \text{olume of lye: 40 mL, Leaching time: 4 h. The boron content of primary and residual slag was analyzed by ICP-AES method. The EEB was defined by Eq. (2)}

\[
\text{EEB} = \left( \frac{\text{Boron amount of primary slag}-\text{Boron amount of residual slag}}{\text{Boron amount of primary slag}} \right) \times 100\% \quad \text{...... (2)}
\]

### 2.3. Analysis and Characterization

The chemical analyses of ludwigite ore and metallized pellet were conducted by Chemical Analysis Center of University of Science & Technology Beijing. The chemical composition of boron-rich slag was analyzed by Central Iron & Steel Research Institute. The chemical analysis of the coal was conducted by China National Coal Quality Supervision and Testing Center. The reactivity of the coal with CO\textsubscript{2} was detected by thermal analyzer (TG-DSC, LINSEIS,
STA PT1600, Germany). The XRD patterns of the samples were detected with a Rigaku diffractometer (DMAX-RB 12 kW) using Cu Kα radiation; the scanning angles were in the range from 10 to 100°(2θ) at a speed of 10°/min. The microstructures of metallized pellets and boron-rich slag were observed by scanning electron microscope (SEM, JEOL JSM-6480A, Japan). The microzone chemical composition was analyzed by energy dispersive spectroscopy (EDS, JEOL JSM-6480A, Japan).

3. Results and Discussion

3.1. Effect of Temperature on the Reduction and Melting Behavior

The general trend of reduction process of ludwigite isothermally reduced by coal at 1 623–1 723 K with a C/O of 1.2 is shown in Fig. 3. It can be observed that the degree of metallization is greatly affected by temperature and the reduction proceeds fast with time. The metallization degrees of the pellets are 60.60%, 64.78% and 80.25% when reduced at 1 623, 1 673 and 1 723 K for 5 min, respectively. It seems that the pellets can achieve a high reducibility at the temperatures.

The reactions in the composite pellets include direct reductions and indirect reductions. The indirect reductions are Fe₃O₄+CO=3FeO+CO₂ (3), FeO+CO=Fe+CO₂ (4), accompanied by the Boudouard reaction of C+CO₂=2CO (5). The direct reductions are 3Fe₂O₃+C=2Fe₃O₄+CO (6), Fe₃O₄+C=3FeO+CO (7), FeO+C=Fe+CO (8), and the reduction of wustite by the dissolved carbon of FeO+[C]=Fe+CO (9), accompanied by the carburization reaction of C=[C] (10). The carbothermic reduction is dominated by the direct reduction at the initial stage of reduction, and it is determined by the indirect reduction together with the Boudouard reaction when the CO partial pressure exceeds a certain value, which is dependent on the temperature. From the result shown in Fig. 2, it can be known that the temperature of fastest reaction of the coal with dioxide is about 1 370 K. The furnace temperature is more than 1 623 K, so the reduction process proceeds very fast. The fine particle size also improves the reduction.

The pellet forms a thick iron shell when reduced at 1 623 K for 15 min, and the metallization degree reaches nearly 95%. It shows that the reduction has reached the final point, but the pellet can’t melt. The reason is that the carburization of the reduced iron is not enough to make it melt. On the contrast, the pellet melts quickly at 1 723 K. There are lots of FeO in the separation slag, so the melting point of the slag decreases and the yield of iron is correspondingly low. When reduced at 1 673 K, the slag and iron separate in a clean manner at 12 min. The content of FeO in the slag decreases from 4.71 wt% to 2.02 wt% if the reduction time increases from 11 min to 15 min. The morphology of the pellets during the reduction process at 1 673 K is listed in Fig. 4. The result shows that the size of the pellet shrinks during the reduction process. The cracks will appear at the beginning, and then disappear in the latter reduction process.

3.2. Effect of C/O (mole ratio) on the Reduction and Melting Behavior

The effect of C/O on the metallization degree of the pellets is studied at 1 673 K. The values of C/O vary from 1.0 to 1.4. The reduction curve is presented in Fig. 5. It shows that the metallization degree increases with the increasing of C/O to some extent. The degrees of metallization are 65.98%, 73.31% and 79.27% at 6 min when the C/O are 1.0, 1.2 and 1.4, respectively. The pellet with C/O of 1.0 is short
of reductant at the later period of the reduction stage. As a matter of fact, when the content of pulverized coal increases, the Boudouard reaction will proceed at a faster rate to provide more reductant CO and the reduction is then improved. Most importantly, the starting melting time (i.e., melting point) of pellets decrease with the increasing of C/O. When the C/O are 1.0, 1.2, and 1.4, the melting points of the pellets are 13, 11 and 10 min, respectively. The variation of the content of FeO and residual carbon in the slag with different C/O at melting point are shown in Table 4. It can be concluded that the appropriate C/O is around 1.2 from the results shown in Table 4. In this condition, the pig iron nugget has a comparatively high yield and the reductant consumption isn’t so much. However, if the C/O is 1.4, the reduction and melting rate of the reduced iron will be much faster. So, the reduced iron melted earlier and the rest FeO melts together with the residual gangue before being reduced completely.

### 3.3. Phase Transformation during Reduction Stage

In the reduction and melting experiment of the ore/coal composite pellet (C/O=1.2), the phases evolution of the samples at the reduction stage are analyzed by XRD. The XRD patterns of the reduced samples are shown in Fig. 6. The experiments are performed at 1 673 K for 1, 2, 3, 4, 5, 6, 7 and 8 min, respectively, until it nearly reaches the melting point. For 0 min (i.e., original coal and iron ore mixture), the sample is dominated by Fe₃O₄. For 1 min, the intensity of Fe₂O₃ decreases and the characteristic peaks of FeO appear. For 2 min, the intensity of Fe₂O₃ becomes so weak that some peaks begin to disappear. The peaks of Fe and (Mg,Fe)₂SiO₄ come into being, although they are very weak. The peaks of FeO become stronger, which has been the main phase in the sample. The XRD pattern of the sample obtained by reduced for 3 min shows that the Fe₂O₃ phase disappears completely, while the Mg₂B₂O₅ phase appears. The mixture of Fe, FeO and (Mg,Fe)₂SiO₄ still exist and the peaks of Fe and (Mg,Fe)₂SiO₄ become more stronger. For the latter samples, the amount of Fe and (Mg,Fe)₂SiO₄ phases are more and more, while the amount of FeO phase is on the contrary. The Mg₂B₂O₅ phase is of small quantity and relatively stable. For the last sample, which is reduced for 8 min, are mainly composed of Fe, FeO, and (Mg,Fe)₂SiO₄ and Mg₂B₂O₅ phases.

From the coexistence of FeO, Fe₂O₃ and Fe at the initial stage of reduction shown in Fig. 6, it can be known that the pellet is a heterogeneous system under the assumption that the diameter of the ore particle is small enough. The temperatures at different locations of the pellet are different under the experiment temperature, i.e., 1 673 K, due to the resistance of heat diffusion in the relatively large pellet. The chemical reactions in the interior regions are delayed. To some extent, it accounts for the fact that the initial step of the reduction reaction is controlled by heat conduction.

### 3.4. Microscopic Examination for the Reduced Pellets

Figures 7(a), 7(c), 7(c) and 7(d) show the cross-sectional SEM images of the pellets reduced at 1 673 K for different time. The chemical analysis can be carried out through an EDS with the SEM. When reduced for 2 min, it is clear that the structure of the pellet is still the homogeneous raw materials mixer. The metallic iron is little and it is too difficult to observe the metallic iron particle. The 3 min reduced sample image exhibited a denser phase, with macropores randomly scattering throughout, which makes the CO diffuse easily though the pellet. The diameter of the metallic iron particle (light gray area) is less than 10 μm and it needs magnify 2 000 times to detect. The islets of reduced iron appear at the contacting points between iron oxide and carbon particles. The main phases of the whole pellet are wustite and gangue. In the 6 min reduced pellet, the metallic iron is easily observed and becomes to aggregate and grows up, some of which circles around the boundary of the coal.

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**Table 4.** Variation of the content of FeO and residual carbon in the slag.

<table>
<thead>
<tr>
<th>C/O (mole ratio)</th>
<th>Melting point (min)</th>
<th>FeO (wt%)</th>
<th>Residual carbon (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>13</td>
<td>12.70</td>
<td>0.28</td>
</tr>
<tr>
<td>1.2</td>
<td>11</td>
<td>4.71</td>
<td>0.32</td>
</tr>
<tr>
<td>1.4</td>
<td>10</td>
<td>7.85</td>
<td>0.40</td>
</tr>
</tbody>
</table>
particles. When the pellet is reduced for 8 min, most of the metallic iron has joined together into big area. It shows the beginning of separation of metallic iron phase from the slag phase at this moment. The coal particles (dark gray area) exist all through the reduction process.

From the results shown in Figs. 7(b), 7(c) and 7(d), the metallic iron formed a shell outside the coal particle. The product shell is denser with the reduction prolonged. It will be increasingly difficult for the diffusion of CO in the shell. So, at the later stage of reduction, the diffusion of CO in the product shell may be the rate-determining step.

3.5. Kinetics Analysis of the Reduction Process

The reduction of iron oxide by solid carbon can be taken as first order reaction.15,16) The relation between overall fractional reduction and rate constant is expressed as follows,

\[-\ln(1 - f) = kt \]

where \( f \) is overall fractional reduction of iron oxide, \( t \) is reduction time (s) and \( k \) is integrated rate constant (s\(^{-1}\)).

The \( f \) is calculated by following equation.

\[ f = 1 - \frac{W_O^t}{W_O^0} \]

Where \( W_O^t \) is the weight of reducible oxygen in pellet, which is reduced for \( t \) min, \( W_O^0 \) is the weight of reducible oxygen in green pellet. All the two parameters are got through chemical analysis. The influence of volatile of coal and burning loss of iron ore on the accuracy of experiment data can be excluded in this way.

The relation plot of \(-\ln(1 - f)\) vs \( t \) at 1 573, 1 623, 1 673 and 1 723 K is shown in Fig. 8. All the lines are nearly straight. It proves that applicability of the equation is good. The gradient of the line is taken as the rate constant \( k \). The value of \( k \) increases with increasing temperature. The \( k \) of different temperatures abides by the Arrhenius Eq. (13).

\[ k = k_0 \left(\frac{E}{RT}\right) \]

where \( k_0 \) is frequency factor (s\(^{-1}\)), \( R \) is ideal gas constant (8.314×10\(^{-3}\) kJ/mol·K), \( E \) is apparent activation energy (kJ/mol), \( T \) is temperature (K).

The Arrhenius plot of the rate constant \( k \) is shown in Fig. 9. The apparent activation energy is 180.17 kJ/mol. The val-
ue is close to the activation energy for the Boudouard reaction: 221.75 kJ/mol \(^{14}\) and diffusion of carbon in \(\gamma\)-Fe: 157 kJ/mol. \(^{17}\) It is still difficult to tell which is the rate-determining step for reduction in ludwigite-coal pellets.

### 3.6. Property of Boron-bearing Iron Nugget

Boron-bearing iron nugget can be got when the pellet (C/O=1.2) is reduced for 15 min at 1673 K. The chemical composition and density of the nugget is presented in Table 5. The results show that the property of the nugget is almost the same with pig iron. It can be good scrap for the melting shop of iron and steel work. Due to the contacting time between iron and slag is short and the thermodynamic difficulty of \(\text{B}_2\text{O}_3\) reduction by carbon, the boron content in the nugget is only 0.065 wt%. However, the content of sulfur is as much as 0.27 wt%, which is higher than the traditional pig iron used for the EAF and BOF steel making. On one hand, it is difficult to desulfurize the nugget in the reduction and melting process of the composite because of the short contacting time and the bad fluidity of iron and slag. On the other hand, the sulfur content is very high in the raw material (\textit{i.e.} ludwigite). It needs further research on the desulfurization method.

The microstructure observed by optical microscope and SEM is shown in Figs. 10(a) and 10(b). The main phase components are pearlite (black area), secondary cementite (white area) and ledeburite (substrate) shown in Fig. 10(a). Boron atom will aggregate in the grain boundary when its content is more than 0.01 wt%. \(^{19}\) It may be the important reason for the easy separation between iron nuggets and graphite crucible in the experiment. The SEM image shows that there are micropores in the substrate of the iron nugget. The micropores may be the hole of monoxide bubble, which is produced at melting stage. Totally speaking, the iron nugget is very clean and there is nearly no oxide inclusion.

### 3.7. Property of Boron-rich Slag

The pellet is heated for 15 min at 1673 K, and then shut down the furnace to make the slag cool slowly in the furnace. The chemical composition of the slag is shown in Table 6. The content of \(\text{B}_2\text{O}_3\) is higher than 20 wt%, and it makes the slag meet the requirements of I grade szaiablyeite ore. \(^{20}\) The total yield of boron is more than 96% through mass balance calculation. Most of the boron is concentrated in the so called boron-rich slag.

The XRD pattern of slow cooling boron-rich slag is shown in Fig. 11. The crystalline phases present in the slag are olivine (\(\text{MgSiO}_3\)), suanite (\(\text{Mg}_2\text{B}_2\text{O}_5\)) and kotoite (\(\text{Mg}_3\text{B}_2\text{O}_6\)), which agrees well with the crystallization rule of \(\text{B}_2\text{O}_3\)–\(\text{MgO}\)–\(\text{SiO}_2\) ternary phase diagram of the same composition. Most of the boron becomes into suanite phase, which can be seen from the diffraction intensity in Fig. 11. The EEB closely depends on the species of crystalline phases and their amounts. The EEB of suanite is higher than kotoite. \(^{21}\) As a matter of fact, boron oxide easily become glass phase, so the cooling route is most important when the composition of the boron-rich has been fixed. The EEB of the slow cooling slag in the study is 86.46%. So, the slow cooling slag crystallizes very well.

SEM image of the slow cooling boron-rich slag sample is shown in Fig. 12. The micrograph reveals that the slag is mainly composed of two phases: dark grey and light grey, except for the white phase of metallic iron. The two phases are nearly of the same amount according to the area fraction of each phase shown in Fig. 12. The EDS analysis of the two phases is also performed, which can help identify all the

<table>
<thead>
<tr>
<th>Table 5. Property of boron-bearing iron nugget.</th>
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<tbody>
<tr>
<td>Composition</td>
</tr>
<tr>
<td>Content/wt.%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6. Chemical composition of boron-rich slag (wt%).</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>Content/wt.%</td>
</tr>
</tbody>
</table>

Fig. 10. Microstructure of boron-bearing iron nugget. (a) Optical microscope image, (b) SEM image.

Fig. 11. XRD pattern of slow cooling boron-rich slag.

Fig. 12. SEM image of the slow cooling boron-rich slag sample.
present phases. The dark and light grey phases are marked as A and B in the image, respectively. The boron can’t be analyzed out, because it is a kind of light elements. The region A consists of approximately 33.23 mole% Mg, 53.92 mole% O, 0.73 mole% Si and 0.55 mole% Fe. It is as if the region A is the crystalline phase of MgO (i.e. periclase), but the phase has not been found from the result of XRD analysis shown in Fig. 11. At last, it can be concluded that region A (dark grey phase) is boron-bearing crystalline phase, most of which is suanite. The region B consists of approximately 21.59 mole% Mg, 45.29 mole% O, 12.47 mole% Si and 0.36 mole% Fe. It is apparent that the region B (light grey phase) stands for olivine.

From the microstructural picture of the boron-rich slag shown in Fig. 12, it is clear that the morphology of the suanite particle is lath-shaped, and most of the olivine phase is similar to square or diamond shape. The embedded features of the two phases are comparatively simple. The grain size of suanite is as large as 50 μm and the size of olivine is even larger. The boron mineral can be easily enriched through a flotation method.

4. Conclusions

(1) The metallization degree and melting morphology of the ludwigite/coal composite pellet strongly depend on temperature. The pellet can’t melt at 1623 K, but the iron and slag separate badly at 1723 K. The appropriate temperature is about 1673 K.

(2) The carbon content affects the metallization degree not as much as melting behavior. The more carbon the pellet contains, the earlier the pellet melts. The yield of iron is not as much as melting behavior. The more carbon the pellet contains, the earlier the pellet melts.

(3) The reduced pellet is a heterogeneous multi-phase system. Heat diffusion in the pellet plays a important role at initial reduction stage. The apparent activation energy of the reduction process is 180.17 kJ/mol.

(4) The iron forms nugget when the pellet is reduced at 1673 K for 15 min. The iron nugget contains 0.065 wt% boron and its property is almost same with the pig iron. The iron nugget is a kind of clean scrap for steelmaking except for (i.e. except for the higher sulfur) the higher sulfur.

(5) The unreduced B₂O₃ and the gangue melt into slag phase. The content of B₂O₃ in the slag is more than 20 wt%.

The crystalline phases of boron-rich slag are olivine (Mg₂SiO₄), suanite (Mg₂B₂O₅) and kotoite (Mg₃B₂O₆). The EEB of the slag is 86.46% if it is cooled appropriately to make the suanite and kotoite crystallize well enough. The slow cooling boron-rich slag is a kind of good raw material for borax and boric acid production.

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