EFFECT OF REDUCTION TEMPERATURE ON THE CARBOtherMIC REDUCTION PROCESS OF LATERITE ORES MIXING WITH BIO-COAL

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Abstract

In this study, carbothermic reduction experiments with different laterite ores mixed with bio-coal were conducted. Different reduction temperatures (900-1400°C) were also used with the carbothermic reduction process to study the direct reduction mechanism. Results show that major phase were Fe₁.₈₃₃(OH)₀.₅O₂.₅ and Fe₂SiO₅ before reduction of limonite. After reduction, the phase was Fe. The major phases were Fe(CO₃), Fe₃O₄, Fe₂SiO₄ and Al₂S₄ before reduction of saprolite. After reduction, the phases were Fe, Fe₀.₆₄Ni₀.₃₆ and α-Fe₀.₀₆Ni. For the reduction, bio-coal had become the reductant. Nickel content of limonite had been raised from 1.18 to 1.64% and the nickel content of saprolite from 3.43 to 4.93%. The observations show that for the carbothermic reduction mechanism of pellet, the outer layer of pellet formed a dense area and the core of pellet had loose area in the initial reduction reaction. When the pellet was produced in the two-phase region at 1200°C, the pellet had a significant shrink. The shrinking rate is 30%. Finally, the pellet formed nickel-iron alloy phase and iron was separated from the oxide phase.

Keywords: Carbothermic Reduction, Laterite, bio-coal

1. INTRODUCTION

Nickel is an important resource. Laterite and sulfide ores are the two main sources of nickel [1-4]. Approximately 30% of the world’s nickel reserves are in the form of sulfide, and 70% are in the form of laterite. The chemical composition of sulfide ore is (Ni, Fe)xSy and those of laterite ore are 2(Mg, Fe)O·SiO2 (olivine) and (Mg, Fe)O·SiO2 (enstatite). Although 70% of the world’s land-based nickel is contained in laterite, it currently accounts for only about 40% of world nickel production. Laterite ores cannot be concentrated like sulfide ores; rather, they must be processed as mined. Therefore, it is vitally important to develop a practical and inexpensive process for refining laterite. Laterite ore has two types, namely limonite and saprolite. Limonite is a low-grade ore, with a nickel content of 1.1-1.8 wt%. Saprolite is a rich ore, with nickel content of more than 2 wt% [5-7]. Nickel can be extracted from laterites via hydrometallurgical or pyrometallurgical processes. Pyrometallurgical processes are relatively more suitable. In this study, pyrometallurgical processes are used to reduce laterite.

With the threat of global warming, many alternative forms of energy have been proposed to replace fossil fuels [8]. Biomass can become solid fuel via torrefaction, which is a thermal pretreatment process in which raw biomass is heated in the temperature range of 200-300 °C in an inert nitrogen atmosphere for several minutes to several hours. After torrefaction, the volatile matter (VM) of bio-coal decreases to 34-85 wt%, whereas its fixed carbon (FC) increases to 13-45 wt% [8-10]. In the present study, limonite and saprolite laterite ores are mixed with bio-coal at various reduction temperatures to determine the effect of reduction temperature on the carbothermic reduction process [9, 10].
2. EXPERIMENTAL PROCEDURE

Laterite ores were dried at 105 °C and crushed to fit through a 0.25-mm screen. The composition of the nickel laterite ores before reduction was determined using chemical analysis, simultaneous thermal analysis (STA), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The laterite ores were mixed with bio-coal at 900-1400 °C for 30 min with a C/O ratio of 0.75 in the carbothermic reduction experiment. The protective atmosphere was argon, whose flow rate was 300 cc/min. After reduction, the samples were examined by XRD, SEM, energy-dispersive X-ray spectroscopy (EDS), and bromin methyl alcoholic solution analysis. The reduction samples were prepared in a high-temperature furnace, as shown in Figure 1.

![Schematic of high-temperature tube furnace](image)

Fig. 1 Schematic of high-temperature tube furnace

3. RESULTS AND DISCUSSION

3.1 Raw Material

3.1.1 Chemical composition analysis

The chemical compositions of the nickel laterites (limonite and saprolite) are shown in Table 1. The elemental analysis results of the bio-coal are shown in Table 2. The results show that the bio-coal is a reductant, whose FC value is 47.1 wt%.

### Table 1 Chemical composition of nickel laterite (wt%)

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Ni</th>
<th>Co</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>TFe</th>
<th>Na₂O</th>
<th>MnO</th>
<th>ZnO</th>
<th>PbO</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limonite</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>1.18</td>
<td>0.16</td>
<td>0.15</td>
<td>4.41</td>
<td>4.50</td>
<td>10.21</td>
<td>41.12</td>
<td>0.02</td>
<td>1.27</td>
<td>0.04</td>
<td>0.01</td>
<td>15.48</td>
</tr>
<tr>
<td>Saprolite</td>
<td>0.01</td>
<td>0.11</td>
<td>0.01</td>
<td>3.43</td>
<td>0.19</td>
<td>0.40</td>
<td>10.84</td>
<td>2.00</td>
<td>10.73</td>
<td>29.41</td>
<td>0.02</td>
<td>1.09</td>
<td>0.08</td>
<td>0.01</td>
<td>25.25</td>
</tr>
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</table>

### Table 2 Elemental analysis of bio-coal (wt%)

<table>
<thead>
<tr>
<th>Bio-coal</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element analysis</td>
<td>47.1</td>
<td>4.06</td>
<td>1.84</td>
<td>31.45</td>
</tr>
</tbody>
</table>

3.1.2 XRD analysis

The XRD patterns shown in Figure 2 reveal that the major phases of limonite were Al₂Si₂O₅(OH)₄ and Fe₁.₈₃₁(OH)₀.₅O₂·₂.⁵; other phases included FeO(OH), Fe(CO₃), and Fe₃O₄. The major phases of saprolite were Fe(CO₃), Fe₃O₄, and Mg(CO₃). In laterite ore, Ni occurs mainly in the form of Mg silicates, and Cr occurs
mainly in the form of Fe silicates or goethite. The mineral species contain crystal water and carbonate and hydroxyl groups. Limonite and saprolite are oxidized nickel laterite.

![Limonite and Saprolite](image)

**Fig. 2 XRD patterns for nickel laterites (a) limonite and (b) saprolite.**

### 3.2 Reduction of laterite

#### 3.2.1. Chemical and XRD analysis

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) results of limonite and saprolite at various temperatures are shown in Table 3 and Table 4. The total nickel of limonite increased from 1.18% (before reduction) to 1.64% (after reduction) and that of saprolite increased from 3.43 to 4.93%.

To observe the structural evolution of the ore as a function of the reduction temperature, the samples were heated at 900, 1000, 1100, and 1200 °C, respectively, for 30 min, and then analyzed using XRD. The diffraction patterns of the limonite ore reduced at various temperatures are given in Figure 3. XRD analysis indicates that the major phases of limonite before reduction were Fe$_{1.83}$(OH)$_{0.8}$O$_{2.5}$ and Fe$_2$SiO$_3$, and that after reduction was Fe. The diffraction patterns of the saprolite ore reduced at various temperatures are given in Figure 4. The major phases of saprolite before reduction were Fe(CO$_3$)$_2$, Fe$_3$O$_4$, Fe$_2$SiO$_4$, and Al$_2$S$_4$, and those after reduction were Fe, Fe$_{6.4}$Ni$_{0.36}$, and α-Fe$_{10.08}$Ni. It is believed that the oxide phase transformed into a metal phase with increasing reduction temperature, and that the bio-coal became a reductant.

#### Table 3 ICP-AES results of limonite at various temperatures

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>0.26</td>
<td>5.34</td>
<td>41.7</td>
<td>4.42</td>
<td>1.07</td>
<td>11.10</td>
<td>1.18</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>900</td>
<td>0.45</td>
<td>3.42</td>
<td>45.1</td>
<td>2.39</td>
<td>0.85</td>
<td>5.84</td>
<td>1.37</td>
<td>1.31</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>1000</td>
<td>0.47</td>
<td>3.53</td>
<td>51.5</td>
<td>2.85</td>
<td>0.97</td>
<td>6.77</td>
<td>1.57</td>
<td>1.88</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>1100</td>
<td>0.47</td>
<td>3.43</td>
<td>54.1</td>
<td>2.38</td>
<td>1.01</td>
<td>6.73</td>
<td>1.64</td>
<td>1.66</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>1200</td>
<td>0.47</td>
<td>3.49</td>
<td>53.6</td>
<td>2.81</td>
<td>0.94</td>
<td>6.67</td>
<td>1.58</td>
<td>1.75</td>
<td>0.01</td>
<td>0.05</td>
</tr>
</tbody>
</table>

#### Table 4 ICP-AES results of saprolite at various temperatures

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>0.43</td>
<td>9.44</td>
<td>29.6</td>
<td>2.57</td>
<td>1.00</td>
<td>13.11</td>
<td>3.43</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>900</td>
<td>0.54</td>
<td>5.34</td>
<td>36.8</td>
<td>1.81</td>
<td>0.94</td>
<td>7.84</td>
<td>4.29</td>
<td>1.80</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>1000</td>
<td>0.62</td>
<td>6.90</td>
<td>39.4</td>
<td>1.97</td>
<td>1.07</td>
<td>8.52</td>
<td>4.62</td>
<td>1.97</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>1100</td>
<td>0.59</td>
<td>7.34</td>
<td>41.8</td>
<td>1.56</td>
<td>0.99</td>
<td>8.91</td>
<td>4.87</td>
<td>2.01</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>1200</td>
<td>0.61</td>
<td>7.62</td>
<td>42.2</td>
<td>1.59</td>
<td>1.04</td>
<td>8.56</td>
<td>4.93</td>
<td>2.00</td>
<td>0.02</td>
<td>0.04</td>
</tr>
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</table>
3.2.2. Cross sections of limonite and saprolite

Cross sections of pellets of laterite mixed with bio-coal at various temperatures are shown in Figure 5. The pellets have two regions at 900 °C, namely a dense outer layer and a loose core. With increasing temperature, the inward diffusion of the dense area led to the gradual disappearance of the loose area. The metallic phase became liquid at the soft melting temperature, and the pellets shrank at 1200-1300 °C. Finally, the pellets formed a nickel-iron alloy phase and iron and oxide phase separation at 1400 °C. The carbothermic reduction mechanism of the pellets is show, the sintering led to the formation of two regions, namely a dense area in the outer layer of the pellet and a loose area in the core of the pellet. When the temperature was increased to 1200 °C, the sintering phenomenon spread to the soft melting temperature. Due to surface energy of the metal phase and oxide phase, produced iron oxide separation at 1400 °C.

Figures 6 to 8 show SEM images of samples obtained at various temperatures. Cross section results shown in Figure 5, after the reduction of nickel laterite roughly divided into three parts. The pellet of laterite has a dense outer layer and a loose core at 900 to 1100 °C. The whole pellet then becomes dense at 1200-1300 °C. Finally, pores form in the core of the pellet at 1400 °C. The SEM images of samples reduced at 1000 °C for 30 min shown in Figure 6 confirm that the outer layer of the pellet became dense after reduction. Because the heat cannot diffuse into the core of the pellet, the core is loose. Phase distribution of pellets with silvery white oxide phase and black carbon phase.
Figure 5 Cross-section images of laterites mixed with bio-coal after reduction at various temperatures

3.2.3. SEM-EDS analysis

SEM images of samples reduced at 1200 °C for 30 min are shown in Figure 7. The reduction of limonite produced a continued metal phase in the outer layer of the pellet, island-like and small spherical metal phases in the core of the pellet, and a black oxide phase and phase composition of carbon in the rest of the pellet. The reduction of saprolite formed island-like and spherical metal phases in the outer layer of the pellet, small spherical metal phases in the core of the pellet, and black oxide and carbon phases elsewhere. The nickel-iron ratio of limonite is higher than that of saprolite, and thus after the reduction of the metal phase have more continuous phenomenon, and saprolite has low nickel-iron ratio, then there after carbothermal reduction experiments has island and spherical metallic phase based. The SEM images show that limonite and saprolite produced spherical metal phases at 1200 °C, representative has occurred at this temperature, the phenomenon of molten metal and produce two-phase region.

SEM images and EDS analysis results of samples reduced at 1400 °C for 30 min are shown in Figure 8. The pellets of limonite and saprolite became Ni-Fe alloy at 1400 °C, with oxide and carbon phases in the pores. The reason for the pellets has been reached soft melting temperature, the difference between the surface energies of metal and oxide phases can produce iron slag separation.
Fig. 7 SEM images of laterites after reduction at 1200 °C for 30 min

Fig. 8 SEM images of (a) limonite and (b) saprolite after reduction at 1400 °C for 30 min and (c) corresponding EDS analysis results

4. CONCLUSION

Limonite and saprolite laterites were carbothermically reduced at various temperatures. In the reductant, bio-coal had become the reductant, the nickel content of limonite increased from 1.18 (before reduction) to 1.64% (after reduction) and that of saprolite increased from 3.43 to 4.93%. The major phases of limonite before reduction were Fe$_{1.83}$O$_{0.5}$H$_{2.5}$ and Fe$_2$SiO$_2$, and that after reduction was Fe. The major phases of saprolite before reduction were Fe(CO$_3$)$_2$, Fe$_3$O$_4$, Fe$_2$SiO$_4$, and Al$_2$S$_4$, and those after reduction were Fe, Fe$_{0.64}$Ni$_{0.36}$, and α-Fe$_{10.08}$Ni. The outer layer of the pellet formed a dense area and the core of the pellet had a loose area in the initial reduction reaction. When the pellet produced a two-phase region at 1200 °C, it significantly shrank by 30%. Finally, the pellet formed a nickel-iron alloy phase and iron and oxide phase separation.

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REFERENCE


