THERMODYNAMIC ANALYSIS ON THE REDUCTION OF IRON AND CHROMIUM IN VANADIUM-EXTRACTED WASTE SLAG BY BIOMASS

In this paper, the feasibility of carbon thermal reduction of vanadium-extracted waste slag with biomass as reducing agent was studied via thermodynamic analysis. The effects of oxygen absorption ratio, temperature and basicity on the reduction results, especially on the recovery of valuable metals (iron and chromium) were discussed emphatically.

Key words: vanadium-extracted waste slag; biomass; thermodynamic analysis; reduction

INTRODUCTION

Vanadium titanomagnetite is one of the main raw materials for smelting valuable metals in metallurgical industry. Vanadium titanomagnetite generates metallurgical slag enriched in vanadium, chromium and iron in smelting process, referred to as vanadium slag. At present, most chemical and metallurgical enterprises only recycle and utilize vanadium from vanadium slag, accounting for 80% of the global vanadium production [1-2]. The process of natritization-water leaching-vanadium extraction is mainly adopted, and the solid waste produced after extraction of vanadium is just vanadium-extracted waste slag, containing a large amount of iron and chromium [3]. So, it is not a good choice in the long run to directly use vanadium-extracted waste slag in industrial products, which leads to waste of valuable metal resources and the existence of highly toxic Cr⁶⁺ [4-5]. Although some metal components can be recycled by leaching to some extent, other metal components can’t be well utilized and the leaching wastewater needs to be further treated. As a kind of renewable energy, biomass not only has large reserve but also all the carbon elements in it come from the carbon dioxide in the atmosphere absorbed by plant photosynthesis. Therefore, compared with coal, biomass can be used for carbon thermal reduction and is considered to be an ideal reducing agent to replace coal to reduce other metals. In this paper, biomass was used to analyze the equilibrium products of carbon thermal reduction according to Gibbs free energy minimum principle.

METHODOLOGY

Raw materials

Vanadium-extracted waste slag selected in this paper is that by water leaching produced from an enterprise in Chengde, China and its components are shown in Table 1.

The biomass used in this paper is peanut shell also from Chengde. Its elemental compositions are shown in Table 2, and proximate analysis in Table 3.

<table>
<thead>
<tr>
<th>Name</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>MnO</th>
<th>Cr₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>49.37</td>
<td>14.93</td>
<td>12.17</td>
<td>8.32</td>
<td>7.58</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>CrO₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>0.60</td>
<td>3.55</td>
<td>1.65</td>
<td>1.09</td>
<td>0.74</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter definition</th>
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</table>

The oxygen absorption ratio (OAR) is defined as Formula (1), which refers to the ratio of the molar amount of carbon and hydrogen in the reducing agent minus the molar amount of oxygen to the molar amount of oxygen in metal oxide in vanadium extraction.

\[
OAR = \frac{T_x + 3/2T_H - T_O}{\text{Content of metal oxide in waste slag}}
\]

<table>
<thead>
<tr>
<th>Biomass</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>5.88</td>
<td>9.32</td>
<td>18.75</td>
<td>66.33</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Moisture</th>
<th>Ash</th>
<th>Fixed carbon</th>
<th>Volatile</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>5.88</td>
<td>9.32</td>
<td>18.75</td>
<td>66.33</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 1 Constituents of vanadium-extracted waste slag/%

Table 2 Elemental analysis of biomass/%

Table 3 Proximate analysis of biomass/%

Parameter definition

The oxygen absorption ratio (OAR) is defined as Formula (1), which refers to the ratio of the molar amount of carbon and hydrogen in the reducing agent minus the molar amount of oxygen to the molar amount of oxygen in metal oxide in waste slag of vanadium extraction.

\[
OAR = \frac{T_x + 3/2T_H - T_O}{\text{Content of metal oxide in waste slag}}
\]

The metallization rate of a metal, Formula (2) is the ratio of the amount of the metal elemental in the reduction product to the total amount of the metal element before reduction (mainly metal oxide) in vanadium-extracted waste slag.

\[
\text{Metallization rate} = \frac{\text{Metal elemental content in the product}}{\text{Total amount of this metal element in waste slag}}
\]
GIBBS FREE ENERGY CHANGE OF MAIN REDUCTION REACTIONS

Under heating conditions, biomass is easily decomposed into solid carbon C and reducing gases such as CO, H₂ and CH₄. Gibbs free energy change (ΔG) diagram of iron oxides reaction with these reductants are shown in Figure 1. When the temperature is lower than 700 °C, iron oxides mainly react with CO to produce lower iron components, and Fe₂O₃ is mainly reduced to Fe₃O₄ by CO. When the temperature is higher than 700 °C, C can reduce all the high-valence iron oxides to Fe, while Fe₂O₃ and FeO cannot be reduced to Fe by CO. When the temperature is higher than 1 000 °C, the reduction of H₂ with high iron oxides can basically occur, except that the reduction of FeO to Fe is relatively difficult. All the reduction reactions by CH₄ can occur at about 700 °C, not to mention higher temperature.

Gibbs free energy change diagram of chromium oxides reaction are shown in Figure 2. When the temperature is higher than 200 °C, high-valence chromium oxides CrO₃ and Cr₂O₃ can be reduced to low-priced chromium oxides and Cr by C, in which the reduction of Cr₂O₃ to Cr requires a high temperature above 1 200 °C. At 0~1 800 °C, CO can reduce CrO₃ to Cr, and other reduction reactions cannot occur. H₂ can reduce CrO₃ to low-valence chromium oxides, but Cr₂O₃ cannot be reduced to low-valence chromium oxides by H₂. CH₄ can reduce CrO₃ to low-valence chromium oxides, and Cr₂O₃ can be reduced to low-valence chromium oxides by CH₄ at a high temperature of 1 400 °C.

ANALYSIS OF EQUILIBRIUM PRODUCTS

Figure 3 show the change of reduction rates of iron and chromium with temperature under different OAR of vanadium-extracted waste slag from peanut shell. When the temperature is between 1 000 °C and 1 300 °C, the iron metallization rate reaches the maximum. As
the temperature continues to rise, the metallization rate of iron decreases gradually. This is because in this temperature range, iron oxides mainly exist in the form of FeO, and the reduction of FeO by CO is an exothermic reaction. Reduction was inhibited by high temperature, resulting in the reduction rate of iron decreasing. With the increase of OAR (the amount of biomass added increases), the iron metallization rate will gradually increase. When the OAR is 3, the reduction effect of biomass reaches a state of saturation, and the continuous increase of OAR will increase the CO produced by biomass pyrolysis, resulting in the decline of iron metallization rate at high temperature. Considering the economic cost, when the temperature is 1 050 °C and the OAR is 3, the iron metallization rate is 99,3 %, which can be considered as an ideal working condition.

For chromium, the metallization rate increases with the increase of the reduction temperature. However, the chromium metallization rate can’t reach 99 % at the OAR of 3~3,5 until the temperature is over 2 000 °C. So, it is not economical to pursue a higher chromium metallization rate while obtaining a higher iron metallization rate. Therefore, the metal reduction rate of iron is mainly considered.

CONCLUSION

In this paper, the thermodynamic analysis of vanadium-extracted waste slag reduced by biomass was discussed.
(1) When the temperature is 1 050 °C, the oxygen absorption ratio is 3, the reduction rate of iron is more than 99 %. When the temperature is 2 200 °C, oxygen absorption ratio is 3,5, the chromium reduction rate is above 99 %.
(2) The reduction path of iron and chromium was preliminarily explored. For iron-containing components, T<550 °C: Fe2O3-Fe3O4-FeO; T≥550 °C: Fe2O3-FeO-Fe. When the temperature is below 1 000 °C, most chromium exists in the form of CrO3, because CrO3 is easily decomposed into Cr2O3 when heated, but Cr2O3 is reduced at a higher temperature. When the temperature is higher than 1 000 °C, Cr2O3 is gradually reduced to Cr. In addition, a small amount of CrC and Cr2C will appear at the temperature of 1 000 °C~2 000 °C, but their content is not high, so the chromium reduction process can be roughly considered as: T<1 000 °C: CrO3-Cr2O3; T≥1 000 °C: CrO3-Cr2O3-Cr.

ACKNOWLEDGEMENT

This research was supported by the Fundamental Research Fund for the Central Universities (N2225043).

REFERENCES


Note: The responsible for English language is H. Q. Xie – China.