Original Article

Separation and recovery of iron and titanium from oxidized vanadium titano-magnetite by gas-based reduction roasting and magnetic separation

Yulei Sui\textsuperscript{a}, Yufeng Guo\textsuperscript{b,*}, Tao Jiang\textsuperscript{b,*}, Guan-zhou Qiu\textsuperscript{b}

\textsuperscript{a} School of Iron and Steel, Soochow University, Suzhou 215000, Jiangsu, China
\textsuperscript{b} School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, Hunan, China

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\textbf{ABSTRACT}

Gas-based reduction roasting magnetic separation process was conducted to separate and recover iron and titanium from oxidized vanadium titano-magnetite (VTM). The effects of reduction temperature, gas composition, reduction time, grinding fineness, and magnetic field intensity on the efficiency of Fe-Ti separation were investigated. Under the condition of reduction temperature of 1050 °C, reduction time of 120 min and gas composition of P(H\textsubscript{2})/P(H\textsubscript{2} + CO) = 0.72, a magnetic product containing 84.5 wt.% total iron with Fe recovery of 93.67% and a non-magnetic product containing 43.46 wt.% TiO\textsubscript{2} with the TiO\textsubscript{2} recovery of 67.12% were obtained. The efficiency of Fe-Ti separation shows a rise first followed by a decline with the increases of P(H\textsubscript{2})/P(H\textsubscript{2} + CO). Theoretical analyses, XRD, and SEM-EDS results demonstrate that H\textsubscript{2} has a higher reduction ability than CO on oxidized VTM while CO makes a better role in promoting the grow of metallic iron particles, which are both crucial for Fe-Ti separation.

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1. Introduction

Titanium plays a considerably important role in the modern industry, which is widely used in aerospace, military, metallurgy, solar cell, pigment and other advanced materials fields [1–3]. As one of the largest of titanium resources in the world, vanadium titano-magnetite represents a valuable raw material for the production of titanium [4]. It is well known that the key to utilizing the valuable resource is efficiently separate Fe and Ti. However, the effective utilization of VTM is limited due to its complicated crystal structure and symbiosis phenomenon of Fe and Ti in the lattice [5,6]. So far, blast furnace (BF) process is the only one method to treat and utilize VTM in industry. However, only iron and vanadium can be extracted in this process and almost all titanium resource remains in slag without effective utilization [7,8]. Moreover, a high percentage of other iron ore need to be added into VTM to prevent the phenomenon of foaming slag in BF process [9].

\textsuperscript{*} Corresponding authors.
E-mails: yfguo@csu.edu.cn (Y. Guo), jiangtao@csu.edu.cn (T. Jiang).
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Many researchers devoted themselves to the comprehensive utilization of VTM and many novel treatment methods have been developed successfully [10–17], “pre-reduction electric furnace smelting process” and “reduction roasting magnetic separation process” are two of most typical non-BF processes. Compared with “pre-reduction electric furnace smelting process”, “reduction roasting magnetic separation process” will realize the separation and recovery of Fe-Ti in the solid state, and avoid the problem of foamed slag in molten state. In addition, “reduction roasting magnetic separation process” has the advantages of low-cost and short process flow. Therefore, it has attracted enormous attention these years.

In a typical reduction roasting magnetic separation process, VTM pellets are reduced by coal at high temperature (1200–1300 °C) for 3–4 h after pre-treatment process. Then the reduced pellets are ground to 0.074 μm or 0.044 μm by a ball mill or rod mill device [13]. Finally, magnetic product and non-magnetic product are separated under a certain magnetic intensity. Normally, the magnetic product can be used as raw material of ironmaking and steelmaking industry, the non-magnetic product was used to produce titanium white [18]. However, coal-based reduction roasting magnetic separation of VTM also face several issues: (i) The low reaction activity of coal result in poor reduction effect of Fe-Ti-bearing minerals, which consequently lead to low efficiency of Fe-Ti separation. (ii) Energy consumption and process cost are too high because of high temperature, long reduction time and high C/Fe ratio during the process. (iii) Coal ash and residual pulverized coal seriously affect the quality of production [19,20]. It is a prospective way to resolve above issues if coal-based reduction can be replaced by gas-based reduction during the reduction roasting magnetic separation process [21–23]. However, to the best of our knowledge, no previous studies regarding to the effects of gas-based reduction on Fe-Ti separation and recovery have been reported.

In this study, gas-based reduction roasting and magnetic separation of oxidized VTM by H2 and CO was investigated, with an emphasis on the effects of the ratio of P(H2)/P(H2 + CO). The research finding will develop comprehensive utilization methods of VTM and provide a basis for gas-based reduction roasting and magnetic separation of all complicated minerals.

### 2. Experimental

#### 2.1. Raw materials

The chemical composition and XRD pattern of the sample are given in Table 1 and Fig. 1. As we can see from Fig. 1, the main mineral phases of oxidized VTM pellets were hematite (Fe2O3) and pseudobrookite (Fe7TiO3). The majority of the oxidized VTM pellets were in the size range of 10–12 mm, and the crushing strength was 2327 N per pellet.

![Fig. 1 – XRD pattern of oxidized VTM pellets.](image)

| Table 1 – Main chemical composition of the oxidized VTM pellets (wt.%). |
|-----------------|-----------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| TFe             | FeO             | TiO2           | V2O5           | SiO2            | CaO             | MgO             | Al2O3           |
| 54.27           | 1.34            | 12.50          | 0.58           | 2.61            | 1.20            | 0.96            | 2.62            |

#### 2.2. Experimental procedure

The oxidized VTM pellets were loaded into a quartz reactor. And then the quartz reactor was placed into a vertical roaster for reduction roasting. The CO-H2 gas inlet is located at the bottom of the quartz reactor as well as the exhaust gas outlet is located at the top of the reactor, as shown in Fig. 2. These oxidized pellets were roasted at different temperature in the various gas-based atmosphere. For each reduction experiment, Equivalent weight pellets were heated to the required temperature and the gas flow rate of the reduction process is 0.3 m3 h⁻¹.
When the reduction time ended, the reduced pellets were cooled to room temperature in an atmosphere of N₂.

Next, roasted products were wet ground in a ball mill at the certain grinding fineness and then processed through a magnetic separator with the certain magnetic field intensity. Two component parts which called magnetic product and non-magnetic product can be got after filtration and drying. The total iron and TiO₂ contents in the magnetic product as well as in the non-magnetic product were analyzed by chemical method.

The metallization rate was calculated by the following mathematics formula:

\[ \lambda = \frac{W_{\text{Fe}}}{W_{\text{FeT}}} \times 100\% \]

where \( \lambda \) is the iron metallization rate of reduced pellets, and \( W_{\text{Fe}} \) is the metallic iron content of reduced pellets, \( W_{\text{FeT}} \) is the TFe of reduced pellets.

The recovery rate of iron and recovery rate of TiO₂ were calculated by the following mathematics formulas.

\[ \delta_{\text{Fe}} = \frac{m_{\text{FeTi}}}{m_{\text{FeT}}} \times 100\% \]

\[ \delta_{\text{TiO}_2} = \frac{m_{\text{TiO}_2}}{m_{\text{TiO}_2}} \times 100\% \]

where \( \delta_{\text{Fe}} \) is the iron recovery in magnetic product, \( m_1 \) is the weight of magnetic product, \( m \) is the weight of reduced pellets, \( \omega_{\text{FeT}} \) is the TFe of magnetic product, \( \delta_{\text{TiO}_2} \) is the TiO₂ recovery in non-magnetic product, \( m_2 \) is the weight of non-magnetic product, \( \omega_{\text{TiO}_2} \) is the TiO₂ content of non-magnetic product, and \( m_{\text{TiO}_2} \) is the TiO₂ content of reduced pellets.

The mineral and compositions of oxidized VTM pellets and reduced products were investigated by X-ray powder diffraction method (Rigaku D/Max 2500) using Cu-Kα radiation (40 kV, 100 mA) at the scanning rate of 4°/min from 5° to 80°. The microstructures of the reduced products were analyzed by scanning electron microscope (SEM-EDS, JEOL JSM-6490LV).

3. Results and discussion

3.1. Effects of reduction roasting process on Fe-Ti separation

3.1.1. Effect of reduction temperature

Oxidized VTM pellets were roasted at various temperatures for 120 min under a gas composition of \( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) = 0.72 \) and then ground to particle size of <0.044 mm accounting for 90 wt.% following separated at the magnetic intensity of 0.08 T. The effects of reduction temperature on Fe-Ti separation and recovery are shown in Fig. 3.

As observed, with the increasing of reduction temperature from 850 °C to 1050 °C, TFe of obtained magnetic product increases from 73.55 wt.% to 84.5 wt.% and the recovery rate of iron increases from 80.33% to 93.67%. Meanwhile, the residual TiO₂ amount in the magnetic product decreases from 13.72 wt.% to 6.52 wt.%. For the obtained non-magnetic product, with the reduction temperature increases from 850 °C to 1050 °C, the TiO₂ amount in non-magnetic product increases from 18.55 wt.% to 43.46 wt.%, TiO₂ recovery rate increases from 33.39% to 67.12%, and the residual amount of Fe decreases from 47.19 wt.% to 17.35 wt.%. The efficiency of Fe-Ti separation and recovery increases slightly as the reduction temperature over 1050 °C.

3.1.2. Effect of gas composition

In the condition of reduction temperature of 1050 °C, reduction time of 120 min, reduced pellets mill to a particle size of <0.044 mm accounting for 90 wt.% and the magnetic intensity of 0.08 T, the effect of \( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) \) on the efficiency of Fe-Ti separation is shown in Fig. 4.

If pellets were reduced by pure CO (\( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) = 0 \)), the efficiency of Fe-Ti separation is poor: the TFe grade and iron recovery are only 75.85 wt.% and 89.21%, respectively, while residual TiO₂ amount is as high as 13.35 wt.%. The separation efficiency of Fe and Ti improved quickly with the increasing of \( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) \). As the ratio of \( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) \) increases from 0 to 0.72, the TFe grade increases by 8.65 wt.%, while iron recovery increases by 4.4 wt.% and residual TiO₂ amount decreases by 6.8 wt.%. However, the TFe grade and iron recovery of obtained magnetic product decrease and the amount of residual TiO₂ increase when the \( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) \) increase to 1. For the obtained non-magnetic product, with the \( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) \) increasing from 0 to 0.72, the TiO₂ amount increases from 22.86 wt.% to 43.46 wt.%, TiO₂ recovery increases from 31.47% to 67.12%, and the residual amount of Fe decreases from 33.84 wt.% to 17.35 wt.%. Meanwhile, TFe grade and iron recovery of the obtained non-magnetic product decreases remarkable when the ratio of \( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) \) was further increased.

3.1.3. Effects of reduction time

In the condition of reduction temperature of 1050 °C, gas composition of \( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) = 0.72 \), reduced pellets mill to a particle size of <0.044 mm accounting for 90 wt.% and the magnetic intensity of 0.08 T, the effect of reduction time on the Fe-Ti separation is shown in Fig. 5.

It can be seen in Fig. 5, as the reduction time increases from 60 min to 120 min, TFe of the obtained magnetic product and Fe recovery increases from 78.21 wt.% to 84.5 wt.% and from 86.06% to 93.67%, respectively. Meanwhile, the amount of TiO₂ of the obtained non-magnetic product increases from 30.50 wt.% to 43.46 wt.%, and TiO₂ recovery increases from 52.62% to 67.12%. In addition, there are no obvious improvements of Fe-Ti separation efficiency if the reduction time was exceeds 120 min.

3.2. Effect of magnetic separation process on Fe-Ti separation

VTM pellets were roasted at the condition of reduction temperature of 1050 °C, gas composition of \( \text{P(H}_2) / \text{P(H}_2 + \text{CO}) = 0.72 \), and reduction time of 120 min. Then the roasted pellets were grounded by ball mill and separated under different magnetic intensity.

3.2.1. Effect of grinding size

The effect of grinding size on the efficiency of Fe-Ti separation was studied by fixing the magnetic field intensity of 0.08 T, and the results are presented in Table 2. With the
Fig. 3 – Effects of reduction temperature on (a) TFe, Fe recovery, and residual TiO₂ amount of obtained magnetic product and (b) TiO₂ amount, recovery of TiO₂, and residual Fe amount of non-magnetic product.

Fig. 4 – Effects of P(H₂/P(H₂ + CO) on (a) TFe, Fe recovery, and residual TiO₂ amount of obtained magnetic product and (b) TiO₂ amount, recovery of TiO₂, and residual Fe amount of non-magnetic product.

Fig. 5 – Effects of reduction time on (a) TFe, Fe recovery, and residual TiO₂ amount of obtained magnetic product and (b) TiO₂ amount, recovery of TiO₂, and residual Fe amount of non-magnetic product.

Table 2 – Effects of grinding fineness on TFe, iron recovery of the obtained magnetic product and TiO₂ amount, recovery of TiO₂ of the non-magnetic product.

<table>
<thead>
<tr>
<th>Magnetic product</th>
<th>Non-magnetic product</th>
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<tbody>
<tr>
<td>Yield/%</td>
<td>TFe/wt.%</td>
</tr>
<tr>
<td>76.49</td>
<td>81.35</td>
</tr>
<tr>
<td>75.60</td>
<td>84.5</td>
</tr>
<tr>
<td>74.35</td>
<td>84.93</td>
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increasing of grinding fineness from 74 μm to 44 μm, TFe of the obtained magnetic product increases from 81.35 wt.% to 84.5 wt.% with the Fe recovery increases from 91.24% to 93.67%; and the amount of TiO₂ of the obtained non-magnetic product increases from 40.73 wt.% to 43.46 wt.% with the TiO₂ recovery increases from 60.61% to 67.12%. Further increases the grinding fineness to 37 μm, TFe of the obtained magnetic product and TiO₂ recovery of the non-magnetic product increase slightly, but Fe recovery of the magnetic product and the amount of TiO₂ of the non-magnetic product present a trend of decrease. Sufficient grinding fineness is necessary for monomer dissociation of minerals but too fine grinding fineness have negative impact on Fe-Ti separation. Therefore, a grinding fineness of 44 μm (particle size of <0.044 mm accounting for 90 wt.%) is recommended for the best.

3.2.2. Effect of magnetic field intensity
Under the condition of grinding fineness of 44 μm. The effect of magnetic field intensity from 0.04 T to 0.16 T on Fe-Ti separation is shown in Fig. 6.

As can be seen in Fig. 6, with the increasing of magnetic field intensity from 0.04 T to 0.08 T, TiO₂ amount of the non-magnetic product, and iron recovery of the magnetic product show an remarkable increase trend while TFe of the magnetic product and TiO₂ recovery of the non-magnetic product shows a slightly decrease trend. Further increase the magnetic field intensity, the TiO₂ amount of the obtained non-magnetic product fall. In addition, an excessively low magnetic field intensity leads to the high amount of iron left in non-magnetic product and an excessively high magnetic field intensity result in a high amount of TiO₂ left in magnetic product, both are disadvantageous to the separation of Fe-Ti. Therefore, the optimal magnetic field intensity was determined to be 0.08 T.

Based on the above results, optimized process conditions obtained by one factor at a time test for Fe-Ti separation from oxidized VTM are as follows: reduction temperature of 1050°C, gas composition of P(H₂)/P(H₂ + CO)=0.72, reduction time of 120 min, grinding fineness of 44 μm (particle size of <0.044 mm accounting for 90 wt.%), and magnetic field intensity of 0.08 T. In this condition, a magnetic product with total iron grade of 84.5 wt.% and iron recovery rate of 93.67% as well as a non-magnetic product with TiO₂ amount of 43.46 wt.% and TiO₂ recovery of 67.12% are obtained.

3.3. Influence mechanisms of gas composition on Fe-Ti separation
Reduction and magnetic separation are two key steps in the treatment process. In order to obtain a high Fe-Ti separation efficiency, iron oxide of VTM ore must be reduced to metallic iron in the reduction roasting step so that Fe and Ti can be separated in the chemical state. Meanwhile, adequate

<table>
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<th>Table 3 – Metallization rate of oxidized VTM pellets under different P(H₂)/P(H₂ + CO).</th>
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<tr>
<td>Gas composition</td>
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<tr>
<td>Metallization rate%</td>
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Fig. 8 – SEM-EDS analysis of reduction pellets samples under atmosphere of $P(\text{H}_2)/P(\text{H}_2 + \text{CO}) = 0$ (a, c, e) and $P(\text{H}_2)/P(\text{H}_2 + \text{CO}) = 1$ (b, d, f): (a) and (b) SEM patterns; (c) and (e) EDS patterns of spot 1 and 2 in (a); (d) and (f) EDS patterns of spot 1 and 2 in (b).
metallic iron size is required to satisfy the monomer separation of metallic iron particles during the magnetic separation process. So, in order to achieve high Fe-Ti separation efficiency, a high metallization rate and a big size of metallic iron particles are both required.

In order to reveal the influence mechanisms of gas composition on Fe-Ti separation, the samples were examined by XRD and SEM-EDS analyses. The XRD patterns of reduced VTM oxidized pellets at different P(H2)/P(H2 + CO) are present in Fig. 7.

As evident in Fig. 7, metallic iron (Fe), titanite magnetite (Fe3−xTi4xO4, 0 < x < 1), and ilmenite (FeTiO3) were main mineral phases in the pellets when the pellets were reduced at CO atmosphere (P(H2)/P(H2 + CO) = 0).

The main reactions are as follows [8,24]:

\[ 3Fe_2O_3 + CO(g) = 2Fe_3O_4 + CO_2(g) \]
\[ Fe_3O_4 + CO(g) = 3FeO + CO_2(g) \]
\[ FeO + CO(g) = Fe + CO_2(g) \]
\[ xFe_2TiO_3 + (1 - x)Fe_3O_4 + xCO(g) = Fe_{3-x}Ti_xO_4 + xCO_2(g) \]
\[ Fe_{3-x}Ti_xO_4 + (4 - 3x)CO(g) = xFeTiO_3 + (3 - 2x)Fe + (4 - 3x)CO_2(g) \]

Mineral phases in the reduced pellets are different if H2 were added to the gas mixture: when the pellets were reduced at the condition of P(H2)/P(H2 + CO) = 0.5, the diffraction intensity of Fe3−xTi4xO4 (0 < x < 1) and FeTiO3 decreased and peaks with associated with new phases of ferropseudoboobrooke (FeTi2O5) appeared, indicating that titanite magnetite and ilmenite were reduced by H2.

\[ Fe_{3-x}Ti_xO_4 + (4 - 3x)H_2(g) = xFeTiO_3 + (3 - 2x)Fe + (4 - 3x)H_2O(g) \]
\[ 2FeTiO_3 + H_2(g) = FeTi_2O_5 + Fe + H_2O(g) \]

All Fe3−xTi4xO4 (0 < x < 1) and FeTiO3 peaks were disappeared when P(H2)/P(H2 + CO) was increased to 0.72. There is no obvious phase transformation when the ratio of P(H2)/P(H2 + CO) was further increased to 1.

The XRD results indicated that H2 has higher reduction activity on oxidized VTM pellets than CO during the process. And metallization rates test in Table 3 also indicates that metallization rates of reduced pellets increased with the increasing of P(H2)/P(H2 + CO). So H2 has a favorable impact on the reduction of oxidized VTM pellets, which is benefit to the Fe-Ti separation in the view of chemical state.

Fig. 8 shows the SEM-EDS images of the reduced under the condition of P(H2)/P(H2 + CO) = 0 and P(H2)/P(H2 + CO) = 1, respectively. As shown in EDS images in Fig. 8, gray area in the mineral particles have a high Fe amount when the pellets were reduced at the condition of P(H2)/P(H2 + CO) = 0, while the Fe amount in gray area was decreased when the pellets were reduced at the condition of P(H2)/P(H2 + CO) = 1. And this is in accordance with XRD analysis.

However, besides the degree of reduction, the size of metallic iron also plays a key role in the following magnetic separation, which directly affect the efficiency of Fe-Ti separation. When the pellets were reduced at the condition of P(H2)/P(H2 + CO) = 0, as we can see from SEM images of Fig. 8, metallic iron particles are aggregated together, and most of the iron particles are grown to more than 20 μm, which was also described in our reported study [24]. While for the pellets which were reduced at the condition of P(H2)/P(H2 + CO) = 1, the metallic iron particles have not formed a combination with one another. And the particles size of most metallic iron particles is less than 10 μm. It must be noted that adequate metallic iron size is required to satisfy the monomer separation of metallic iron particles during the magnetic separation process, and higher particles size leads to higher efficiency of Fe-Ti separation.

The difference of particles size of most metallic iron during different gas atmosphere can be attributed to the number of crystal nucleus and thermodynamics. The reduction ability and the reduction rate of H2 is higher than CO in the temperature range of experiment, so the number of new-born iron crystal nucleus in the beginning of H2 reduction process is more. More number of new-born iron crystal nucleus leads to smaller size of metallic iron particles. In addition, researchers found that the total thermal effect of oxidized VTM in CO atmosphere is exothermic but opposite in H2 atmosphere [25]. So, the heat would be accumulated inside the pellets when the pellets were roasted in CO atmosphere, which improved the diffusion and crystallization of newly formed metallic iron.

All in all, H2 has a favorable impact on the reduction of oxidized VTM pellets, which is benefit to the Fe-Ti separation in the view of chemical state. However, the particles size of most metallic iron particles is less than 10 μm when the pellets were reduced by H2. So H2 has an unfavorable impact on the physical separation of Fe-Ti. To the contrary, CO has a favorable impact on the growth of iron particles, which is benefit to the physical separation of Fe-Ti. But the samples reduced by CO have a low metallization rate due to the low reduction activity. So, the highest Fe-Ti separation should be achieved in an appropriate CO-H2 mixture gas atmosphere. And that is why the efficiency of Fe-Ti separation showed a rise first followed by a decline with the increased of P(H2)/P(H2 + CO).

4. Conclusions

(1) The separation between Fe and Ti of VTM could be achieved by gas-based reduction followed by magnetic separation. Under the condition of reduction temperature of 1050°C, reduction time of 120 min, gas composition of P(H2)/P(H2 + CO) = 0.72, reduced pellets mill to a particle size of <0.044 mm accounting for 90 wt.% and the magnetic intensity of 0.08 T, a magnetic product containing 84.5 wt.% total iron and a non-magnetic product containing 43.46 wt.% TiO2 were obtained, with Fe recovery of 93.67% and TiO2 recovery of 67.12%.

(2) The efficiency of Fe-Ti separation shows a rise first followed by a decline with the increases of P(H2)/P(H2 + CO). And that is because H2 exhibit a higher reduction ability than CO on oxidized VTM during the experiment while CO makes a better role in promoting the grown of metallic iron particles. So appropriate H2-CO mixture has a better performance on Fe-Ti separation than pure H2 or CO during gas-based reduction roasting magnetic separation process.
Conflicts of interest

The authors declare no conflicts of interest.

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