1. Introduction

Vanadium titanomagnetite (VTM) is recognized as a strategic resource throughout the world.1-3) The Hongge VTM (HVTM) that located in Panxi region of China, is one of the largest VTM resources, besides iron, titanium, and vanadium, there is high content of chromium. The chromium reserve is 900 Mt, accounting for approximately 68% of Chinese total chromium reserve.4,5) Therefore, the utilization of this complex iron ore is imperative.

At present, the blast furnace (BF) has been utilized for smelting VTM to produce hot metal and high-titanium slag with the content of TiO$_2$ varying from 22% to 25%, which cannot be effectively utilized through traditional processes and leads to serious environmental pollution.6-8) In the past years, several new processes based on coal-based direct reduction for the comprehensive utilization of VTM or HVTM have been conducted.9-19) Wu et al.9) investigated the influences of smelting temperature, smelting time, and the basicity of metallized pellet on vanadium and iron recovery. Zhao et al.12) surveyed the reduction behavior of FeO-V$_2$O$_3$ and FeO-Cr$_2$O$_3$ during coal-based direct reduction of HVTM. However, the recovery rates of vanadium, titanium, and chromium are still low in these processes. In addition, the coal-based direct reduction will cause practical production problems, such as high energy consumption and narrow operating temperature range.20) Therefore, HVTM has not been exploited and effectively utilized on a commercial scale.

In order to utilize HVTM efficiently, a novel clean smelting process has been developed by the authors’ group, which evidently increases the recovery rates of valuable elements.21) In this process, the gas-based direct reduction of oxidized HVTM pellet (HVTMP) is an essential procedure, no matter BF or gas-based shaft furnace, the application of HVTMP as a burden presents many advantages, such as uniform size, high physical strength, and low degradation.22) Numerous studies on the gas-based direct reduction of HVTM or VTM were carried out.23-29) Li et al.23) investigated the correlations between roasting characteristics of HVTMP and its subsequent reduction behaviors. Pan et al.27) studied the reduction behavior of raw and oxidized VTM in a bubbling fluidized bed. As mentioned previously, the contents of Cr$_2$O$_3$ in these studies were lower than 1.5 wt%, and it is uncertain whether Cr$_2$O$_3$ affects the gas-based direct reduction of HVTM especially under condition of relatively higher content of Cr$_2$O$_3$ with simulated shaft furnace gases. Hence, it is necessary to understand the influence of Cr$_2$O$_3$ on the gas-based direct reduction behavior.
and mechanism of HVTMP in order to utilize HVTM more effectively.

As an integral part of ongoing work to develop a novel clean smelting process of HVTM, the focus of this research was to investigate the reduction behavior and mechanism of HVTM with different Cr$_2$O$_3$ additions with simulated shaft furnace gases, and deeply clarify the reduction degree, phase transformation, morphology, and reduction swelling. These findings could provide both theoretical and technical basis for the effective comprehensive utilization of HVTM in shaft furnace.

2. Experimental

2.1. Materials

In this work, the HVTM was sourced from the Panxi-Honge region of China. The chemical composition is listed in Table 1. From Table 1, it could be known that the HVTM has a low total iron content and middle TiO$_2$ content. Figure 1 shows the X-ray diffraction (XRD) patterns of HVTM. The main mineral compositions were magnetite (Fe$_3$O$_4$), titanomagnetite (Fe$_{2.75}$Ti$_{0.25}$O$_4$), coulsonite (Fe$_2$VO$_4$), and chromite (FeCr$_2$O$_4$). The Cr$_2$O$_3$ used in the experiments was analytical reagent grade.

2.2. Procedure

2.2.1. Oxidation Roasting Experiment

The HVTMP with different Cr$_2$O$_3$ additions was prepared by the following procedures. First, HVTM was homogeneously milled with Cr$_2$O$_3$ and bentonite in a planetary ball mill for 2 h at a rotating speed of 200 rpm, the mixture was then mixed with water and balled into green pellets in a disc pelletizer. The mass ratios of Cr$_2$O$_3$ addition to the HVTM were controlled as 0 wt%, 4 wt%, 8 wt%, and 12 wt%, respectively. The green pellets with diameter between 11.5 and 12.5 mm were dried in an oven at 105°C for 5 h. Oxidation roasting experiments were carried out in a muffle furnace. When the preheating temperature (900°C) was reached at a heating rate of 10°C/min, air was continuously purged to the muffle furnace to provide oxidizing ambience, and then the dried pellets were placed in the furnace. After preheating for 10 min, the temperature was increased up to the roasting temperature. The roasting temperature and time were set to 1200°C and 20 min, respectively. Eventually, the roasted pellets were removed from the furnace and cooled to room temperature in the absence of air.

2.2.2. Gas-based Direct Reduction Experiment

The gas-based direct reduction of HVTMP was conducted in a reduction shaft furnace shown in Fig. 2. For the reduction experiment, the HVTMP were placed in the furnace when the furnace reached the desired reduction temperature under a nitrogen atmosphere. Then, the nitrogen flow was switched to the reducing gas of simulated HYL-III from the bottom of reactor to start the reduction, the gas compositions were 64.3%H$_2$ + 25.7%CO + 5%CO$_2$ + 5%N$_2$ gas mixtures. The weight of HVTMP could be monitored continuously and recorded in real-time by the connected computer, and the gas flow rates were 4 L/min in all cases. After the desired time ended, the reduced pellets were quickly removed from the furnace and put into the cooling container to room temperature under the protection of a high flow rate of argon atmosphere.

In this study, the reduction degree (R) is calculated according to following formula:

$$R = \left[ \frac{0.11w_1}{0.43w_2} + \frac{m_1 - m_0}{m_0w_2 \times 0.43} \right] \times 100\% \quad \ldots \ldots (1)$$

where $w_1$ is the ferrous content in the oxidized pellet; $m_1$ is the initial mass of pellet after removal of moisture; $m_0$ is the mass of pellet after each time $t$; $w_2$ is the content of total iron before reduction; $m_0$ is the initial mass of pellet; 0.11 is the necessary conversion factor of corresponding amount of oxygen making FeO oxidized to Fe$_2$O$_3$; 0.43 is the conver-

![Fig. 1. XRD patterns of HVTM.](image1)

Table 1. Chemical composition of HVTM (wt%).

<table>
<thead>
<tr>
<th>TFe</th>
<th>FeO</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>V$_2$O$_5$</th>
<th>Cr$_2$O$_3$</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.54</td>
<td>26.25</td>
<td>0.98</td>
<td>4.88</td>
<td>2.98</td>
<td>2.50</td>
<td>9.26</td>
<td>0.62</td>
<td>1.48</td>
<td>0.48</td>
<td>0.01</td>
</tr>
</tbody>
</table>

![Fig. 2. Schematic diagram of experimental apparatus.](image2)
sion factor of corresponding amount of oxygen making all total Fe oxidized to Fe₂O₃.

The degree of metallization degree of reduced HVTMP is calculated as follows:

\[
\text{Metallization degree} = \frac{M_{Fe}}{T_{Fe}} \times 100\% \quad \ldots (2)
\]

where \(M_{Fe}\) is the mass fraction of metallic iron and \(T_{Fe}\) is the mass fraction of total iron after reduction.

The volume swelling index is defined as follows:

\[
\text{Swelling index} = \frac{(V_a - V_o)}{V_o} \times 100\% \quad \ldots (3)
\]

where \(V_a\) is the volume of the pellets after reduction and \(V_o\) is the volume of the pellets before reduction.

2.3. Characterization

The compressive strength and reduction swelling were measured according to the ISO 4700 and ISO 4689:2007, respectively. A mercury injection apparatus was used to determine the porosity. The phase composition was investigated by X-ray diffraction (XRD). The chemical composition of reduced HVTMP was evaluated using inductively coupled plasma optical emission spectrometry (ICP-OES). The morphology was analyzed by scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS). The measuring position in the pellets was at a depth of 3 mm from the outside to the inside of the cross sections of the pellets with different Cr₂O₃ additions.

3. Results and Discussion

3.1. Characterization of HVTMP with Different Cr₂O₃ Additions

The porosity of HVTMP with different Cr₂O₃ additions is shown in Fig. 3. From Fig. 3, it could be found that the porosity gradually increased with the increase of Cr₂O₃ addition. Besides, the microstructure of HVTMP with 0 wt% and 12 wt% Cr₂O₃ additions is shown in Fig. 4. For the HVTMP with 0 wt% Cr₂O₃ addition, it could be seen that grains formed a dense structure and coalesced to each other, only a few pores existed among the grains. When the Cr₂O₃ addition was 12 wt%, the microstructures tended to be porous with the development of large pores which were not homogeneously distributed across the sample. The size of dense grains decreased and presented in small grains, which meant that the addition of Cr₂O₃ had negative effect on the connection among the grains and inhibited the induration of HVTMP.

3.2. Reduction Degree

The reduction curves of HVTMP with different Cr₂O₃ additions obtained at 1 050°C with simulated gases of HYL-III are shown in Fig. 5. Generally, it showed that the reduction of HVTMP was greatly affected by Cr₂O₃ addition and stopped at different extends depending on the Cr₂O₃ addition. In order to clarify the effect of Cr₂O₃ addition on the reduction process more clearly, the trends of reduction degree for different reaction moments are described in Fig. 6. It could be observed that at the early stage of reduction up to 30% (Fig. 6(a)), the addition of Cr₂O₃ promoted the reduction and the reduction rate proceeded faster than those without Cr₂O₃ additions, which was attributed to the increased original porosity of HVTMP with Cr₂O₃ addition shown in Fig. 3. Moreover, the reduction rate increased with the increase of Cr₂O₃ addition. At the intermediate stage of reduction shown in Fig. 6(b) (30–70% reduction degree), the addition of Cr₂O₃ revealed different effects on the reduction depending on its content. The Cr₂O₃ addition of 4 wt% retarded the reduction and this retardation effect increased with the increase of reduction degree. As the Cr₂O₃ addition increased to 8 wt%, a relative decrease in this retardation effect was observed at a given reduction time. However, when the Cr₂O₃ addition was 12 wt%, the reduction degree was higher than that without Cr₂O₃ addition. At the final
stage of reduction shown in Fig. 6(c) (>70% reduction degree), the Cr$_2$O$_3$ addition retarded the reduction and this retardation effect decreased with the increase of Cr$_2$O$_3$ addition. Besides, it should be noted that the final reduction degree decreased with the increasing Cr$_2$O$_3$ addition.

The effect of Cr$_2$O$_3$ addition on the metallization degree of reduced HVTMP for 60 min is shown in Fig. 7. As presented in Fig. 7, under the constant reduction conditions, the Cr$_2$O$_3$ addition had negative impact on the final metallization degree of reduced HVTMP. The metallization degree was significantly decreased with the increase of Cr$_2$O$_3$ addition from 0 wt% to 4 wt% and without a larger change tendency over 4 wt%. For example, the metallization degree of reduced HVTMP with 0 wt% and 4 wt% Cr$_2$O$_3$ additions were 91.05% and 81.46%, respectively, and further decreased to 79.24% when the Cr$_2$O$_3$ addition was 12 wt%.

3.3. Phase Composition

In order to investigate the phase transformation of reduced HVTMP with various Cr$_2$O$_3$ additions, the phase components of reduced products for 60 min were identified by XRD and the results are shown in Fig. 8. When reduced without Cr$_2$O$_3$ addition, it was obvious that the reduced HVTMP exhibited high content of metallic iron and small amount of TiO$_2$, which was consistent with our previous study.\textsuperscript{21} When 4 wt% Cr$_2$O$_3$ was added, the peaks...
of TiO₂ disappeared, while those of Fe₃Cr₂O₄ and FeTiO₃ were observed. In order to investigate the interpretation of this phenomenon, the phase composition of HVTMP with 4 wt% Cr₂O₃ addition was investigated by XRD and shown in Fig. 9. It was found that the main phase compositions were Fe₂O₃, Fe₅TiO₁₅, (Fe₀.₆Cr₀.₄)₂O₃, Fe₀.₇Cr₁.₃O₃, and (Cr₀.₁₅V₀.₈₅)₂O₃. In the subsequent reduction process of HVTMP with simulated shaft furnace gases, the transformations of Cr-rich phases were shown as follows.

\[(\text{Fe₀.₆Cr₀.₄})₂\text{O₃} = 0.4\text{Cr}_₂\text{O₃} + 0.6\text{Fe}_₂\text{O₃} \quad (4)\]

\[\text{Fe}_₇\text{Cr}_₁\text{O}_₃ = 0.65\text{Cr}_₂\text{O₃} + 0.35\text{Fe}_₂\text{O₃} \quad (5)\]

\[(\text{Fe₀.₁₃V₀.₈₅})₂\text{O₃} = 0.15\text{Cr}_₂\text{O₃} + 0.85\text{V}_₂\text{O₃} \quad (6)\]

\[\text{Fe}_₂\text{O₃} + 3\text{Cr}_₂\text{O₃} + \text{H}_₂ = 3\text{FeCr}_₂\text{O}_₄ + \text{H}_₂\text{O} \quad (7)\]

\[\text{Fe}_₂\text{Cr}_₂\text{O}_₄ + \text{CO} = \text{Fe}_₂\text{Cr}_₂\text{O}_₄ + \text{CO}_₂ \quad (8)\]

When reduced without Cr₂O₃ addition, the Cr-bearing phases were not found in the final reduced HVTMP, which was resulted from the relatively low content of chromium in HVTMP and the limitations of the analysis method. However, when 4 wt% Cr₂O₃ was added, more solid solutions were formed and changed into Fe₃Cr₂O₄ and the content of Cr-bearing phases increased. The chemical reactions and thermodynamic calculations of the reduction of Fe₃Cr₂O₄ by H₂ and CO were investigated by Factsage 7.0 reaction module and shown as follows.

\[\Delta G^0 = 80581.95 - 24.83T (J/\text{mol}) \quad (9)\]

\[\Delta G^0 = 54518.81 + 5.98T (J/\text{mol}) \quad (10)\]

From the thermodynamic calculations, it could be found that the standard Gibbs free energies of the two chemical reactions were greater than zero under the experimental temperature; therefore, Fe₃Cr₂O₄ was difficult to be reduced by H₂ and CO and remained unreacted in the final reduced HVTMP, and the peaks of Fe₃Cr₂O₄ were observed. The presence of Fe₃Cr₂O₄ prevented the further reduction of FeTiO₃. Besides, it also showed that the peak intensity of metallic iron was significantly decreased, which was mainly attributed to the suppressed metallization degree by the formation of Fe₃Cr₂O₄ and FeTiO₃ and it was in agreement with Fig. 7. With the increasing Cr₂O₃ addition, the peak intensities of Fe₃Cr₂O₄ and FeTiO₃ became stronger, while those of metallic iron became weaker, which was consistent with the change of metallization degree.

### 3.4. Morphology Change

The SEM images of the cross sections of reduced HVTMP with different Cr₂O₃ additions were studied in order to characterize the growing character of metallic iron particles during gas-based direct reduction, and the results are shown in Fig. 10. The measuring position in the reduced HVTMP was at a depth of 3 mm from the outside to the inside of the cross sections. It was easy to see that the HVTMP without Cr₂O₃ addition was reduced better than those with Cr₂O₃ additions. When reduced without Cr₂O₃ addition, many white metallic iron particles could be observed and the metallic iron grains had been combined with each other with a larger size. Besides, the slag phases also associated with each other closely. These results showed that the separation of metallic iron phases and slag phases was perfect during the reduction process without Cr₂O₃ addition.

When the Cr₂O₃ addition was 4 wt%, it showed clearly that the structure of metallic iron particles was destroyed and dispersed obviously, which indicated that the growth and connection of metallic iron particles were suppressed by the addition of Cr₂O₃. In addition, the EDS analysis indicated that the metallic iron particles (white) contained a small amount of chromium and most of chromium remained in the slag phases. Combined with the XRD results in Fig. 8, it could be found that this phase was Fe₃Cr₂O₄ that connected with Ti-rich phases and remained in the slag phases. Since Fe₃Cr₂O₄ was thermodynamically stable under the reduction conditions in this study, it will not be reduced further. The chromium will remain in the slag phases instead of entering into the metallic iron phases and the chromium content in the metallic iron was extremely low, the further reduction of Ti-rich phases was prevented and the peaks of FeTiO₃ were observed.

When the Cr₂O₃ addition was increased to 8 wt%, the chromium content of slag phases increased compared to that adding 4 wt% Cr₂O₃. Therefore, the majority of chromium was in the form of Fe₃Cr₂O₄ instead of being reduced and transferred into the metallic iron phases. The borders between metallic iron particles and slag phases were obvious and the further reduction was prevented, which resulted in the low final reduction degree, although the addition of Cr₂O₃ promoted the reduction rate at initial stage. When reduced with 12 wt% Cr₂O₃ addition, the size of metallic iron particles further decreased and only part of them eventually aggregated and connected with each other. The scattered trend of metallic iron particles was more obvious.

Figures 11 and 12 show the valuable elemental distribution mapping micrographs of reduced HVTMP with 0 wt% and 12 wt% Cr₂O₃ additions, respectively. It further confirmed that the iron element was relatively more dispersed with the increase of Cr₂O₃ addition and most of the chromium
remained as FeCr$_2$O$_4$ in the slag phases instead of entering into the metallic iron phases.

3.5. Reduction Swelling and Compressive Strength

The effect of Cr$_2$O$_3$ addition on reduction swelling index and compressive strength of reduced HVTMP is shown in Fig. 13. As shown in this figure, the addition of Cr$_2$O$_3$ significantly affected the reduction swelling index and compressive strength. The reduction swelling index increased from 12.95% to 19.58% when the Cr$_2$O$_3$ addition increased from 0 wt% to 8 wt%, however, the compressive strength decreased from 469.08 N to 202.06 N correspondingly. The increase in the reduction swelling index corresponded to the decrease in the compressive strength. They exhibited a reversed linear relationship as shown in Fig. 14 and the experimental linear regression equation was:

$$ C = -26.81S + 784.72 $$

(11)

where $C$ is the compressive strength and $S$ is the reduction swelling index of reduced HVTMP.

To further investigate the reason for the increase of reduction swelling with different Cr$_2$O$_3$ additions, the morphology of reduced HVTMP at 60 min was analyzed and given in Fig. 15. It showed that Cr$_2$O$_3$ addition had an obvious influence on the inner structures and number and size of metallic iron whiskers. For the reduced HVTMP without Cr$_2$O$_3$ addition (Fig. 15(a)), it could be found that the morphology was dense, clustered metallic iron whiskers were formed on the surface and connected with each other, which corresponded to lower reduction swelling. As discussed in 3.1, the HVTMP was compact and had low porosity without Cr$_2$O$_3$ addition, which prevented the growth of metallic whiskers in subsequent reduction process and resulted in the low reduction swelling.

When the Cr$_2$O$_3$ addition was 4 wt% (Fig. 15(b)), more metallic iron whiskers were formed and changed the dense morphology to porous structure and separated the particles. This phenomenon was attributed to the fact that the HVTMP with Cr$_2$O$_3$ addition had loose microstructure and high porosity. Metallic iron whiskers succeed in pushing the
Fig. 11. The map scanning analysis of reduced HVTMP with 0 wt% Cr$_2$O$_3$ addition.

Fig. 12. The map scanning analysis of reduced HVTMP with 12 wt% Cr$_2$O$_3$ addition.

Fig. 13. Effect of Cr$_2$O$_3$ addition on the compressive strength and reduction swelling index of reduced HVTMP.

Fig. 14. Relationship between reduction swelling index and compressive strength of reduced HVTMP.
Figure 15. SEM morphology of reduced HVTMP with different Cr$_2$O$_3$ additions. (a) 0 wt%; (b) 4 wt%; (c) 8 wt%; (d) 12 wt%.

adjacent grain in the reduction process, which resulted in higher reduction swelling. With the increase of Cr$_2$O$_3$ addition (Figs. 15(c) and 15(d)), a large number of metallic iron whiskers were formed and grew in a highly porous structure. The formed metallic iron whiskers further separated the particles and increased the distances among the particles, making the particles become more porous and caused higher reduction swelling. The change in the morphology was consistent with the variation in the reduction swelling in Fig. 13.

4. Conclusions

To clarify the important influence of Cr$_2$O$_3$ addition on the gas-based direct reduction behavior and mechanism of HVTMP with simulated shaft furnace gases, oxidation roasting and reduction experiments were conducted. The following conclusions were drawn:

1. Cr$_2$O$_3$ had an obvious effect on the reduction degree and rate of HVTMP and the reduction process could be divided into three stages. When Cr$_2$O$_3$ was added, FeCr$_2$O$_4$ was easily formed, which was hard to be reduced and prevented the further reduction of FeTiO$_3$, eventually having an adverse effect on the final metallization degree.

2. With the increasing Cr$_2$O$_3$ addition, the number and size of metallic iron particles gradually decreased and only part of them eventually aggregated and connected with each other. Besides, most of chromium still remained as FeCr$_2$O$_4$ in the slag phases instead of being reduced and entering into the metallic iron phases.

3. The reduction swelling and compressive strength of HVTMP were significantly affected by Cr$_2$O$_3$ addition. With the increase of Cr$_2$O$_3$ addition, a large number of metallic iron whiskers were formed and further separated the particles, which accompanied by porous structure and resulted in the increasing reduction swelling. In addition, the reduction swelling had relationship with the compressive strength of reduced HVTMP with different Cr$_2$O$_3$ additions.

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