Effect of $V_2O_5$ Addition on Oxidation Induration and Swelling Behavior of Chromium-Bearing Vanadium Titanomagnetite Pellets with Simulated Coke Oven Gas Injection into Blast Furnace

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The study discusses the oxidation induration and swelling behavior of chromium-bearing vanadium titanomagnetite pellets (CVTP) with $V_2O_5$ additions, and the reduction swelling index (RSI) and compressive strength (CS) of reduced CVTP were investigated with simulated coke oven gas (COG) injection into the blast furnace (BF). The results show that the CS of CVTP decreases and the porosity of CVTP increases with increasing $V_2O_5$ additions. The proportion of microsize pore size distribution of CVTP between 0 to 5 $\mu$m decreases notably while the pore size distribution between 5 to 30 $\mu$m increases with increasing $V_2O_5$ additions. The $V_2O_5$ mainly exists in the form of $V_2TiO_5$ and $V_{1.93}Cr_{0.07}O_3$ in CVTP and $V_2TiO_5$ in reduced CVTP. The V-bearing spinels on the grain boundaries with fragmented and prismatic structure restrain the CS of CVTP. The CS of reduced CVTP decreases and RSI increases with increasing $V_2O_5$ additions. The $V_2O_5$ addition facilitates the aggregation and diffusion of metallic iron particles, and the shape of the metallic iron whiskers transform round dot to prismatic. The pores and intervals enlarge, and thickness of lamellar crystals thickens gradually with increasing $V_2O_5$ additions. The study could supply the theoretical and technical basis for the utilization of CVTP and other V-bearing ores with COG recyclable technology.

KEY WORDS: $V_2O_5$; oxidation induration; reduction swelling index; coke oven gas; chromium-bearing vanadium titanomagnetite pellets.

1. Introduction

Blast furnace (BF) is widely used in the ironmaking process and has been the primary ironmaking method. Nevertheless, the massive utilization of coke and coal in BF generates plenty of carbon monoxide (CO) and carbon dioxide (CO$_2$). The CO$_2$ emission from iron and steel industry is equivalent to about 15% of the whole CO$_2$ emission in China. At present, the idle coke oven gas (COG) is more than 65 million m$^3$ every year in a big iron and steel industry. The average heating value of COG is 18 500 kJ/m$^3$. Hence, COG is a kind of valuable fuel to decrease the usage of coal and coke in BF. Besides, the COG contains 60.7% H$_2$, and the COG injection is recognised as one of the viable methods to decrease CO$_2$ emission and for low carbon ironmaking in BF.

The chromium-bearing vanadium titanomagnetite (CVTM) in the Sichuan–Panzhihua area in China is a large reserve resource, and the reserve is more than 3.5 billion tons. The CVTM is one of the largest vanadium titanomagnetite (VTM) mineral resources which have V, Cr, and many other rare elements.1,2) The grade of V in the Hongge mine reaches 0.57%. Similar types of ores are mainly distributed in Russia, Canada, Australia, and other places in the world.3,4) As it is known, many studies have been done for the sintering of CVTM, while the studies on the rare elements of CVTM are scarce.5,6) Owing to the unresearched and preindustrial technology of CVTM in the BF process, the study of CVTM is necessary.

Mousa7) studied the influence of COG injection on the BF with isothermal and nonisothermal reduction of sinter under different gas compositions and temperatures, and the reduction rate can be increased with COG injection under isothermal condition. Liu8) considered that the operation of COG injection into BF could increase hot metal productivity and decrease coal ratio, coke ratio, and carbon emission of BF. Wang9) investigated the mathematical simulation on BF operation of COG injection, and the indirect reduction degree increases due to the involvement of hydrogen in the cohesive zone with COG injection. Further, the productivity and CO utilization efficiency increase and CO$_2$ emission and energy consumption decrease with COG injection. Nishioka10) considered that the COG was available and stable as a kind of hydrogen source in the industry. Meanwhile, the COG has been successfully carried out in BF in the COURSE50 project. Mousa11) studied that the reduction rate of pellets increased sharply with COG.

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Tang\cite{12} investigated that product V$_2$O$_3$ grains dispersed in V$_2$O$_5$ pellets which restricted the diffusion among lattices and the growth of mineral grains, and then decreased the CS of V$_2$O$_5$ pellets. Meanwhile, the hematite grains in V$_2$O$_5$ pellets were with shape of sharp corners resulting in big crystal active and heterogeneous surface activity, and then the metallic iron generates partly and grows directionally because of the heterogeneous activity and different nucleation ability of grain surface during the reduction leading to the increasing RSI of V$_2$O$_5$ pellets. Yang\cite{13} studied that the increase of porosity promoted the reduction condition of CVTM sinters. Hence, the porosity of pellet is an improtant characteristic in the reduction process. He\cite{14} studied the distributions of titanium, vanadium, and chromium on the iron and slag in the smelting of CVTM in BF due to the specific reactions of valuable components. Li\cite{15} studied that the addition of V$_2$O$_5$ promoted the reduction rate of iron ore to iron carburization due to the catalytic effect of reduced metallic iron on methane cracking which accelerates the reduction and carburization of iron ore. Roshchin\cite{16} studied the reduction of Fe from the iron-vanadium concentrates, and vanadium and chromium are fixed by titanium oxides and are not present in both of residual magnetite and metallic phase. Zhao\cite{17} studied the reduction behavior of Fe$_2$VO$_4$ and FeCr$_2$O$_4$ during the direct reduction of VTM. Li\cite{18} investigated that the addition of V$_2$O$_5$ weakens the compact structure of pellets due to the restrictive recrystallization and grain growth of hematite. In the present studies on VTM, many scholars researched the properties and smelting mechanism of pellets on BF and gas-based shaft furnace.\cite{12,13,14} The V$_2$O$_5$ as the one of the main valuable compositions in CVTM, but the few studies have been conducted on the RSI of CVTP with simulated COG, and more characteristics including porosity and pore size distribution on oxidized CVTP are measured to enrich oxidation mechanism of CVTP with V$_2$O$_5$ addition.

In this study, the effect of V$_2$O$_5$ addition on the phase compositions, compressive strength, porosity, microstructure, and oxidation induration of CVTP were first analysed. Further, the impact of V$_2$O$_5$ addition on reduction swelling behavior of CVTP with simulated COG injection into BF was investigated. These results will provide theoretical and technical bases for the production of CVTP and other V-bearing minerals with COG injection technology.

2. Materials and Methods

2.1. Materials

The CVTM stems from the Hongge (Sichuan, China). The chemical compositions of the CVTM are listed in Table 1. Figure 1 shows the XRD pattern of the CVTM. The main minerals of the CVTM are Fe$_3$O$_4$, FeTiO$_3$, and Fe$_{2.75}$Ti$_{0.25}$O$_4$. The other peak intensities of Fe$_2$VO$_4$ and FeCr$_2$O$_4$ are weak. The V$_2$O$_5$ was of analytical grade purchased from Sinopharm Chemical Reagent Co. (China).

| TFe | FeO | TiO$_2$ | V$_2$O$_5$ | Cr$_2$O$_3$ | CaO | SiO$_2$ | MgO | Al$_2$O$_3$ | P | S |
|-----|-----|-------|---------|--------|-----|-------|-----|---------|---|---|
| 53.35 | 26.91 | 11.60 | 0.57 | 0.81 | 0.96 | 4.71 | 3.33 | 2.82 | 0.02 | 0.26 |

2.2. Apparatus and Procedure

The pelletizing process includes mixing, balling, drying, oxidation induration, and cooling. The main parameters of pelletizing process include 8.0% moisture of mixing materials, 30 min of pelleting time, 10–12 mm size of green pellets, 105°C of drying temperature for 5 h, 900°C of preheating temperature for 20 min, and 1 200°C of roasting temperature for 20 min with 1.5 L/min blowed air. The CVTP was taken out of the muffle furnace and cooled to ambient temperature when oxidation induration was finished.

The swelling behavior of the CVTP was studied in comprehensive metallurgical measuring apparatus, as shown in Fig. 2. The constant temperature zone of stainless steel reaction tube (75 mm diameter and 900 mm length) is marked with red band. First, the 18 CVTP with average size 10–12.5 mm were placed into the constant temperature zone of the apparatus and heated to the target temperature in the N$_2$ atmosphere with 3 L/min. Then, middle COG injection (150 m$^3$/THM, CO–H$_2$–CO$_2$–N$_2$=40–15–10–35 Vol.%) was purged into the apparatus with 15 L/min. Finally, the reactor was removed from the apparatus and cooled in the N$_2$ atmosphere when the reduction was completed. The reduction swelling index (RSI) and compressive strength of reduced CVTP were measured. The reduction temperature was 900°C and time was 60 min.
The RSI is defined as follows:

\[
RSI = \frac{V_t - V_0}{V_0} \times 100\% \quad \cdots (1)
\]

Where the \( V_0 \) and \( V_t \) are the volumes of original CVTP and reduced CVTP, respectively, mm\(^3\). The diameters of the CVTP and reduced CVTP were measured through an electronic vernier calliper.

### 2.3. Analytical Methods

The X-ray fluorescence (XRF, ZSXPrimus II; Rigaku, Japan) was used to test the chemical compositions of raw materials. The X-ray diffraction (XRD, X’ Pert Pro; PANalytical, Almelo, Netherlands) with Cu K\(\alpha\) radiation (wavelength = 1.5406 Å) at a setting of 40 kV and 40 mA was used to analyze the mineral phases of CVTM and CVTP. The scanning electron microscope (SEM, Ultra Plus; Carl Zeiss GmbH, Jena, Germany) was used to detect the microstructure of CVTP with backscattering detector (BSE) and energy disperse spectroscopy (EDS). The porosity and pore size distribution of CVTP were tested by mercury injection apparatus (Micromeritics Instrument Corporation, Autopore IV 9500, USA). The compressive strength (CS) of CVTP and reduced CVTP was referred to ISO4700. The RSI of reduced CVTP was referred to ISO4698.

### 3. Results and Discussion

#### 3.1. Oxidation Induration of CVTP

**3.1.1. Phase Composition**

The oxidation induration process of CVTP includes a series of physical-chemical reactions. **Figure 3** shows the primary phases of CVTP with different V\(_2\)O\(_5\) additions. It is revealed that the primary phases of CVTP without V\(_2\)O\(_5\) addition are Fe\(_2\)O\(_3\) and Fe\(_2\)TiO\(_5\). As the V\(_2\)O\(_5\) addition increases from 2 to 6 mass%, the 2\(\theta\) values of V\(_2\)O\(_3\), V\(_2\)TiO\(_3\), and V\(_1.93\)Cr\(_{0.07}\)O\(_3\) peak further increases and 2\(\theta\) values of Fe\(_2\)O\(_3\) and Fe\(_2\)TiO\(_5\) peak decrease slightly, hence, the peak intensities of V\(_2\)O\(_3\), V\(_2\)TiO\(_3\), and V\(_1.93\)Cr\(_{0.07}\)O\(_3\) strengthen gradually while the peak intensities of Fe\(_2\)O\(_3\) and Fe\(_2\)TiO\(_5\) weaken with increasing V\(_2\)O\(_5\) additions. It indicates that the content of V\(_2\)O\(_3\), V\(_2\)TiO\(_3\), and V\(_1.93\)Cr\(_{0.07}\)O\(_3\) increases while Fe\(_2\)O\(_3\) and Fe\(_2\)TiO\(_5\) decrease. The main oxidation reactions and phase transformation of Fe\(_2\)O\(_3\), FeTiO\(_3\), and Fe\(_2\)VO\(_4\) in CVTP can be written as:

\[
\begin{align*}
4\text{Fe}_2\text{O}_3 + \text{O}_2 & = 6\text{Fe}_2\text{O}_3 \quad \cdots (2) \\
2\text{Fe}_2\text{O}_3 + 4\text{FeTiO}_3 + \text{O}_2 & = 4\text{Fe}_2\text{TiO}_5 \quad \cdots (3) \\
2\text{Fe}_2\text{O}_3 + 2\text{FeO} + \text{Fe}_2\text{O}_3 + \text{V}_2\text{O}_3 & = 2\text{Fe}_2\text{VO}_4 \quad \cdots (4) \\
\text{V}_2\text{O}_3 + 3\text{Fe}_2\text{TiO}_3 & = \text{V}_2\text{Ti}_2\text{O}_9 + 3\text{Fe}_2\text{O}_3 \quad \cdots (5) \\
19.3\text{V}_2\text{O}_3 + 0.7\text{Cr}_2\text{O}_3 & = 20\text{V}_{1.93}\text{Cr}_{0.07}\text{O}_4 \quad \cdots (6)
\end{align*}
\]

Further, the additive V\(_2\)O\(_5\) react with Fe\(_2\)O\(_3\) to generate V\(_2\)O\(_3\) and Fe\(_2\)O\(_3\), and then the V\(_2\)O\(_3\) reacts with Fe\(_2\)TiO\(_3\) to generate V–Ti solid solution, and Cr\(_2\)O\(_3\) to generate V–Cr solid solution during the oxidation process. According to the thermodynamic calculation of V\(_2\)O\(_3–\)TiO\(_2\) system, three compounds including V\(_2\)TiO\(_5\), V\(_2\)TiO\(_3\), and V\(_2\)TiO\(_4\) form in the oxidation process.\(^{19}\)

#### 3.1.2. Compressive Strength and Porosity

**Figure 4** shows the changes of CS and porosity of CVTP with different V\(_2\)O\(_5\) additions. All error bars represent the standard error of the mean, and the numbers of the repeated experiments of CS and porosity of CVTP are 12 and 4, respectively. The CS decreases from 2 448 to 1 275 N and porosity increases from 14.86% to 22.65% with increasing V\(_2\)O\(_5\) additions. It is observed that V\(_2\)O\(_5\) addition decreases the CS obviously, and the high CS with low porosity is obtained for CVTP without V\(_2\)O\(_5\) addition.

Based on the empirical equation between porosity and CS\(^{20}\)

\[
C = K \cdot d^{-\alpha} \cdot \exp(-\eta \cdot P) \quad \cdots (7)
\]

where C is the compressive strength (N), P is the porosity of the CVTP (%), \( d \) is grain radius (cm), \( K \), \( \alpha \), and \( \eta \) are coefficients.

Equation (8) shows the CS decreases with increasing porosity. Orowan\(^{21}\) studied the equation of theoretical fracture strength of the solid material \( \sigma_t \).

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*Fig. 3. XRD patterns of CVTP with V\(_2\)O\(_5\) additions. (Online version in color.)*

*Fig. 4. Effect of V\(_2\)O\(_5\) additions on the compressive strength and porosity of CVTP. (Online version in color.)*
\[ \sigma_{th} = \sqrt{\frac{E\gamma_s}{r_0}} \] ........................ (8)

where \( E \) is the elastic modulus (Gpa), \( \gamma_s \) is the free surface energy (J), and \( r_0 \) is the average distance between atoms (nm).

Spriggs\(^2\) studied the effect of porosity on elastic modulus as the following equation

\[ E = E_0 \cdot \exp(-\beta \cdot P) \] ........................ (9)

where \( E_0 \) is the elastic modulus nonporous sample and \( \beta \) is an empirical constant.

Hence, the relationship between theoretical fracture strength and porosity is

\[ \sigma_{th} = \sqrt{\frac{E_0 \cdot \gamma_s}{r_0 \cdot \exp(\beta \cdot P)}} \] ........................ (10)

Based on the Eq. (11), theoretical fracture strength decreases exponentially with increasing porosity. It means that theoretical fracture strength decreases with more pores in pellets. Hence, the porosity increases while the CS decreases with \( V_2O_5 \) addition.

According to the histograms, Fig. 5 shows the effect of different \( V_2O_5 \) additions on the pore size distribution of CVTP. The microsize pore size distribution of CVTP mainly distributes between 0 \( \mu m \) to 5 \( \mu m \) when \( V_2O_5 \) addition is lower than 2 mass\%, and the proportion of microsize pore size distribution of CVTP decreases obviously with increasing \( V_2O_5 \) additions, reflecting the incremental intrusion of mercury in microsize pore size decreases continuously. Meanwhile, the pore size increases markedly in a large range from 5 \( \mu m \) to 30 \( \mu m \) with increasing \( V_2O_5 \) additions, which corresponds to the increasing porosity from 14.86\% to 22.65\%. Based on the decreasing CS of CVTP and the negative correlation relationship of CS and porosity, the oxidation induration of CVTP weakens with \( V_2O_5 \) addition. Hence, the porosity of CVTP increases due to the expense of the increasing size of macropores and large size of pores with increasing \( V_2O_5 \) additions.

### 3.1.3. Microscopic Structure

Figure 6 shows the microstructure of CVTP detected by SEM with different \( V_2O_5 \) additions. Based on the XRD analysis of CVTP with \( V_2O_5 \) addition, the \( V_2O_5 \) mainly exists as the form of \( V_2O_3 \), \( V_2Ti_3O_9 \), and \( V_{1.93}Cr_{0.07}O_3 \) on the phase composition of CVTP during the oxidation induration process, showing that the high melting points of V-spinels form on the oxidation induration of CVTP. Meanwhile, no peaks of \( V_2O_5 \) are identified on the \( V_2O_5 \) addition range of 2–6 mass\% due to the most part reaction of \( V_2O_5 \) with \( Fe_3O_4 \), \( Fe_2TiO_5 \), and \( Cr_2O_3 \). Hence, the microstructure of CVTP with different \( V_2O_5 \) additions should be investigated to study the effect of vanadium on mineragraphy and structure of CVTP. Figure 6(a) shows the microstructure of CVTP without \( V_2O_5 \) addition and intervals between grains are distinct with little-closed pores which correspond to the low porosity, and the grain size distribution is relatively uniform. Meanwhile, the gangue mineral exists among the individual hematite grains. Further, the silicate phases mainly act as binder phases among the hematite grain boundaries to form a continuous structure and decrease cracks, corresponding to the relatively high CS of CVTP without \( V_2O_5 \) addition. When 2 mass\% \( V_2O_5 \) is added, many small and square...
shaped grains including hematite and V-bearing spinels exist among the intervals of big hematite grains, as shown in Fig. 6(b). The porous structure is adverse to the strength between adjacent hematite grains due to the little necks and bridges among small mineral grains. The irregular huge and small hematite grains are observed in the Fig. 6(b). Based on the analysis of point A, unsolvable V-bearing spinels and Fe–Ti compound distribute along the grain boundaries. The necks and bridges are restrained to generate and develop among grains during the oxidation induration process. It is obvious that big hematite grains are broken with loose structure and square grains in the intervals, leading to the porous structure. Hence, the CS of CVTP decreases, and porosity of CVTP increases with 2 mass% addition of V₂O₅. The addition of V₂O₅ indicates the adverse effect on the bonding of hematite grains and decomposition trend of huge hematite grains.

Further, the sizes of hematite grains decrease and pore size increases when the V₂O₅ addition increases to 4 mass%. Figure 6(c) shows the macro-grain boundaries, small cracks of hematite grains, and fragmentized and prismatic V-bearing spinel grains. The uneven grains exist in the intervals and separate neighbouring mineral grains. The distribution of V-bearing spinels on grain boundaries restrains the growth and recrystallisation of hematite grains. Based on the analysis of point B, the silk shape of V–Cr spinel and calcic compound exist on the grain boundary of hematite, and the incompact structure is detrimental to the CS of CVTP. Hence, the CS of CVTP deteriorates, and porosity of CVTP enhances with 4 mass% V₂O₅ addition. When the V₂O₅ addition increases to 6 mass%, the microstructure of CVTP is loose and porous with dispersive hematite grains and V-bearing spinels. More cracks and intervals distribute along the grain boundaries, and small pores exist among the unconsolidated structure. Moreover, cracks and lacunae silicate phases exist among small mineral grains.

Figure 7 shows the EDS analysis of CVTP with 6 mass% V₂O₅ addition. From point A to point C, the contents of...
V₂O₅ are 0.27, 0.63, and 35.84 mass%, respectively. Based on the EDS of point A, the dark grey area is silicate phase concentrating Si, Al, and Ca, and little vanadium infiltrates into silicate phase. According to the EDS of point B, the light grey area is compound of hematite and little Fe–Ti compound. Some pores distribute around the silicate grain and connect loosely with adjacent grains. With the analysis of point C, the French grey area is V-bearing spinels with broken structure. The V₂O₅ addition leads to the porous structure with rough grains among hematite grains, V-bearing spinels, and silicate phases, which restrains the crystal growth and recrystallization of hematite in the oxidation induration of CVTP. Moreover, the effect of small V-bearing spinels inhibits the bonding effect silicate phases, as shown in point A of Fig. 7(a). The cracks and small V-bearing spinels are harmful to the improvement of CS while these structures are beneficial to the increasing porosity of CVTP.

Figure 8 shows the elemental distributions of CVTP with 6 mass% V₂O₅. It can be observed that the elemental
distributions of Fe, Si, Ti, V, and Cr in Fig. 8. From Fig. 8, it indicates that V mainly exists on the small mineral grains with a porous structure and some individually tiny particles in intervals of mineral grains, and Cr mainly exists on iron oxides. Hence, V mainly exists on small grains and intervals while Cr mainly distributes on iron oxide grains. The distribution of V has the main effect on strength and structure of CVTP. The Si exists on the silicate phases as the constitution of bonding structure between small hematite grains and V-bearing spinels, and the bonding action decreases among the hematite grains. According to the above analysis, the addition of V2O5 damages the microstructure and recrystallization of hematite grains and increases the porous structure of CVTP during oxidation induration, and finally results in the decreasing CS of CVTP.

3.2. Induration Mechanism

According to the above results, the V2O5 addition has an inhibiting effect on the recrystallization of hematite grains, grain size, and damages the effect of bonding phases, and increases the loose structure in the intervals of mineral grains. Figure 9 shows the schematic diagrams of oxidation induration mechanism of CVTP. The hematite grains are large-grained and interconnected and distribute relatively uniform without V2O5 addition. Further, the hematite grains fully recrystallize and connect, and bonding phases exist at the intervals of grains, which enhance the CS of CVTP.

Nevertheless, the size of mineral grain decreases and the loose and porous of V-bearing spinels fill the intervals of grains. The V2O5 mainly reacts with elements of Ti to generate V2TiO3, and Cr to generate V1.93Cr0.07O3 on the grain boundaries. The V2O5 addition inhibits the connection and size of hematite grains and increases the porous intervals, and the growth and recrystallization of hematite grains are restrained. Hence, V2O5 addition is disadvantageous to the oxidation induration of CVTP and decreases the CS of CVTP.

3.3. Swelling Behavior of CVTP

3.3.1. Thermodynamic Analysis

The main reactions as following take place when CVTP is reduced by simulated COG injection into BF:

\[ 3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \quad \text{(11)} \]
\[ 3\text{Fe}_2\text{O}_3 + \text{H}_2 = 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \quad \text{(12)} \]
\[ \text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2 \quad \text{(13)} \]
\[ \text{Fe}_3\text{O}_4 + \text{H}_2 = 3\text{FeO} + \text{H}_2\text{O} \quad \text{(14)} \]
\[ \text{Fe}_2\text{O}_3 + 4\text{CO} = 3\text{Fe} + 4\text{CO}_2 \quad \text{(15)} \]

\[ \text{Fe}_3\text{O}_4 + 4\text{H}_2 = 3\text{Fe} + 4\text{H}_2\text{O} \quad \text{(16)} \]
\[ \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2 \quad \text{(17)} \]
\[ \text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O} \quad \text{(18)} \]
\[ \text{V}_2\text{Ti}_3\text{O}_8 + 2\text{V}_2\text{O}_3 = 3\text{V}_2\text{TiO}_5 \quad \text{(19)} \]
\[ \text{Fe}_2\text{TiO}_3 + \text{CO} = \text{Fe}_2\text{TiO}_4 + \text{CO}_2 \quad \text{(20)} \]
\[ \text{Fe}_2\text{TiO}_3 + \text{H}_2 = \text{Fe}_2\text{TiO}_4 + \text{H}_2\text{O} \quad \text{(21)} \]

The reduction reactions of iron oxides comply with three stepwise reaction mechanisms when the reduction temperature is 900°C, and the reactions are carried out by three steps: Fe2O3→FeO→Fe. Long23 studied that the three reduction stages of iron oxides are from Fe2O3 to FeO, from FeO to FeO, and from FeO to Fe. Under the similar COG injection, the H2 reduction ratios (the reduction ratio of iron oxides with H2 reduction in the indirect reduction) of iron oxides in the three reduction stages are 7.1%, 60%, and 68%, respectively. Hence, the reduction of manganese or iron oxides belongs to the stepwise reaction. In the solid-state reduction process of CVTP, the reactions between Fe2O3, V2Ti3O8, Fe2TiO5, CO, and H2 belong to the gas-solid reaction. Based on the above results, the preferential reduction reaction of Fe2O3 occurs as Eqs. (11)–(18), and the further reactions of Fe–Ti spinel and V–Ti spinel take place as Eqs. (19)–(21). Based on the phase diagram of TiO2–V2O5 under reduction conditions, the V2Ti3O8 phase can react with V2O5 to V2TiO5 phase due to the dissolution of Ti3+ cations in V-rich phase.19)

3.3.2. Phase Composition

Figure 10 shows the XRD patterns of CVTP reduced for 60 min with different V2O5 additions. The XRD pattern shows the gradual change in the peak with V2O5 addition, indicating the addition of V2O5 has some influence on the phase composition of reduced CVTP. The primary phases of reduced CVTP without V2O5 addition are Fe, FeO, and Fe2TiO3. Further, the peak intensity of the new phase of V2TiO5 strengthens with an increase of V2O5 addition, and the reduction reactions of iron oxides comply with three stepwise reaction mechanisms when the reduction temperature is 900°C, and the reactions are carried out by three steps: Fe2O3→FeO→Fe. Long23 studied that the three reduction stages of iron oxides are from Fe2O3 to FeO, from FeO to FeO, and from FeO to Fe. Under the similar COG injection, the H2 reduction ratios (the reduction ratio of iron oxides with H2 reduction in the indirect reduction) of iron oxides in the three reduction stages are 7.1%, 60%, and 68%, respectively. Hence, the reduction of manganese or iron oxides belongs to the stepwise reaction. In the solid-state reduction process of CVTP, the reactions between Fe2O3, V2Ti3O8, Fe2TiO5, CO, and H2 belong to the gas-solid reaction. Based on the above results, the preferential reduction reaction of Fe2O3 occurs as Eqs. (11)–(18), and the further reactions of Fe–Ti spinel and V–Ti spinel take place as Eqs. (19)–(21). Based on the phase diagram of TiO2–V2O5 under reduction conditions, the V2Ti3O8 phase can react with V2O5 to V2TiO5 phase due to the dissolution of Ti3+ cations in V-rich phase.19)
new phase may have effects on the physical characteristics of reduced CVTP. Liu studied that the Fe$_2$TiO$_4$ was one of the reduced products of iron titanium with H$_2$. Meanwhile, the peak intensity of Fe decreases slightly and the peak intensities of Fe$_2$TiO$_4$ and V$_2$TiO$_5$ increase with the addition of V$_2$O$_5$. The new phase of V$_2$TiO$_5$ is the reduction product of V$_2$Ti$_3$O$_9$, with the above thermomechanical analysis. The chromium element was not detected by XRD due to the effects of crystal and concentration level.

3.3.3. Effect of Time and V$_2$O$_5$ Addition on RSI

The physical stability of CVTP in BF is an important factor in the reduction process. The RSI and CS are the important physical characteristics of reduced CVTP. The swelling behavior with simulated COG injection into BF at 900°C with different time was studied, and results are shown in Fig. 11. The numbers of the repeated experiments of CS and RSI of reduced CVTP are 12 and 3, respectively. Figure 11 shows the different reduction stages in the reduction swelling behavior of reduced CVTP. The RSI of CVTP can be separated into three stages which include initial stage, intermediate stage, and the final stage. In the initial stage, the RSI increases rapidly with increasing time and reach the peak value of 8.45% at 15 min. Moreover, the RSI decreases gradually in the intermediate stage with increasing time. Further, the RSI decreases relaxedly as a smooth curve in the final stage with increasing time. Finally, the RSI reaches 5.87% at 60 min. The intermediate stage and final stage indicate the shrinkage of CVTP after 15 min which is believed to be the sintering of iron whiskers and grains. Hence, the maximum swelling of CVTP is 15 min at the reduction temperature of 900°C. Sharma investigated that the reasons including sintering of iron whiskers and pores and formation of silicate phases most possibly leads to the shrinkage. These phenomena restrict the growth and crystallization of iron whiskers in the structure of reduced pellet and result in the shrinkage of pellets.

Figure 12 indicates the effect of V$_2$O$_5$ addition on the RSI and CS of reduced CVTP with simulated COG injection into BF. The RSI increases from 5.87% to 11.32% while the CS decreases from 901 to 436.4 N with increasing V$_2$O$_5$ additions. Sharma studied that the effect of oxidation induration on the swelling behavior of pellets, and the increasing CS and decreasing porosity of pellets result in the decreasing RSI. Hence, the CS and porosity of pellets influence the RSI of pellets. The low swelling pellet is mainly due to the presence of slag bonds which are not able to push the adjacent grains mechanically and leads to the decrease of volume. Moreover, the generation of iron whiskers during reduction leads to more stresses in pellets and makes the high swelling and less CS of CVTP. The initial high porosity of pellets indicates the fast reduction and less swelling. In the past, the swelling of pellets usually reaches a maximum value at about 900°C by CO at the temperature range of 800–1 100°C because of the formation of a mass of whiskers at about 900°C. Yi studied that the addition of H$_2$ on reduction atmosphere decreased the swelling and expansion characteristic of pellets which showed higher CS of pellets because the pellets passed the wüstite stage rapidly and the bonding of pellets was remarkably improved.

3.3.4. Microscopic Structure

To reveal the mechanism of swelling behavior and CS of reduced CVTP, the microstructures of reduced CVTP with different V$_2$O$_5$ additions were detected, and the results are shown in Fig. 13. It can be indicated that the V$_2$O$_5$ addition has a prominent effect on the microstructures of reduced CVTP. As shown in Fig. 13(a), the microstructure of reduced CVTP is reticular and filiform, and metallic iron whiskers exist in the reticular structure. Hence, the generation of metallic iron whiskers results in the reticular structure and swelling of CVTP. Figure 13(b) shows that the more round dot and short metallic iron whiskers generate on the surfaces of lamellar grains as the formation of the cellular structure when the V$_2$O$_5$ addition is 2 mass%. The lamellar microstructure of CVTP with 2 mass% V$_2$O$_5$ is dense than the CVTP without V$_2$O$_5$ addition. When the V$_2$O$_5$ addition increases to 4 mass%, the metallic iron whiskers and round dot of metallic iron grow gradually, and lamellar crystals thicken by degrees. Further, the intervals and the pores become larger than the CVTP with 2 mass%.
addition, and some metallic iron particles aggregate on the intervals. Moreover, the swelling speed of CVTP decreases slightly when the V₂O₅ addition is 6 mass%, as shown in Fig. 12. From the partial enlarged images of Fig. 13(d), some neighbouring lamellar grains assemble to thicker lamellar minerals. The intervals of lamellar grains are filled with prismatic metallic iron particles, and the dense iron particles aggregate together on the surface of lamellar minerals. The thick metallic iron particles enlarge the interval of the adjacent lamellar minerals, and pores and intervals become the largest when V₂O₅ addition increases to 6 mass%. Hence, the RSI of CVTP increases gradually with increasing V₂O₅ addition, as shown in Fig. 12. The generation of metallic iron whiskers is restrained and the shape of metallic iron changes from round dot to prismatic with increasing V₂O₅ addition. As is shown in the microstructure of reduced CVTP, a large number of metallic iron whiskers are detected without V₂O₅ addition. When the V₂O₅ addition is higher than 2 mass%, the microstructure of reduced CVTP generates nucleation points of metallic iron particles and the aggregation and diffusion of metallic iron enhance the intervals and thickness of lamellar crystals leading to the further swelling behavior. Wang²⁹ studied the swelling behavior of iron ore during the reduction process, and the metal iron whisker as crucial factor caused the swelling. Hence, the V₂O₅ addition facilitates the swelling of CVTP and restrains the increasing CS of CVTP.

3.4. Discussion

Based on the results of oxidation induration and swelling behavior of CVTP, the V₂O₅ additions have obvious effect on the properties of CVTP and reduced CVTP. The CS and structure of CVTP have the impact on the swelling behavior of CVTP during the reduction process with COG injection into BF. The phase compositions, CS, porosity, and microstructure of CVTP were tested and analyzed, and the existences of V-bearing spinels on the grain boundaries with fragmentized and prismatic structure and some individually tiny particles restrain the CS of pellets. Hence, the V₂O₅ addition leads to the fragmentized and loose structure and increasing porosity of CVTP. Further, the CS of reduced CVTP decreases and RSI increases with increasing V₂O₅ additions. The swelling and shrinkage of the reduced CVTP occur concurrently during the reduction process with COG injection. The increasing V₂O₅ addition facilitates the aggregation and diffusion of metallic iron particles, and the metallic iron whiskers decrease with V₂O₅ addition. The
thickness of lamellar crystals thickens gradually with the generation of prismatic metallic iron particles.

4. Conclusions

(1) The primary phases of CVTP with V2O5 addition are Fe2O3, Fe2TiO5, V2O3, V2Ti3O9, and V1.93Cr0.07O3. The CS of CVTP decreases from 2 448 to 1 275 N and porosity increases from 14.86% to 22.65% with increasing V2O5 additions. The CS and CVTP exhibit a negative correlation relationship.

(2) The microsize pore size distribution of CVTP mainly distributes between 0 to 5 μm when V2O5 addition is lower than 2 mass%, and the proportion of microsize pore size distribution of CVTP decreases notably and the pore size distribution of CVTP between 5 to 30 μm increases when V2O5 addition is higher than 4 mass%. The existences of V-bearing spinels on the grain boundaries with fragmented and prismatic structure restrain the strength of pellets.

(3) The primary phases of reduced CVTP with V2O5 addition are Fe, FeO, V2TiO5, and Fe2TiO4. The RSI of reduced CVTP increases rapidly with increasing time, and reach the peak value of 8.45% at 15 min, then RSI decreases to 5.87% as a smooth curve with increasing time.

(4) The RSI of reduced CVTP increases from 5.87% to 11.32% while the CS of reduced CVTP decreases from 901 to 436.4 N with increasing V2O5 additions. The V2O5 addition facilitates the aggregation and diffusion of metallic iron particles, and the shape of the metallic iron whiskers transform round dot to prismatic. The thickness of lamellar minerals thickens gradually, and pores and intervals enlarge with increasing V2O5 additions.

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