Swelling Behavior of High-Chromium, Vanadium-Bearing Titanomagnetite Pellets in H$_2$-CO-CO$_2$ Gas Mixtures

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In this study, the effects of temperature, gas composition and reduction degree on the reduction swelling index (RSI) of high-chromium vanadium-bearing titanomagnetite (HCVT) pellets during reduction with H$_2$-CO-CO$_2$ gas mixtures are investigated. The results show that the formation of massive wüstite causes most of the volume expansion of the pellets. The swelling of HCVT pellets is intensified with the temperature and content of CO, and the RSI reaches a maximum at the reduction degree of 35–50%. In H$_2$/CO = 5/2 (volume ratio) with a temperature range from 1223 K to 1373 K, the maximum RSI increases from 14.68% to 22.54%. Nevertheless, when the ratio of H$_2$/CO increases from 2/5 to 5/2 at 1223 K, the maximum RSI of the pellets decreases from 21.25% to 19.55%. Meanwhile, the shrinking rate of the pellets also decreases from 33.20% to 27.26%.

INTRODUCTION

As a vital carrier of vanadium, titanium, and chromium, high-chromium, vanadium-bearing titanomagnetite (HCVT) has a rich reserve in China and a high comprehensive utilization value. Currently, the main process to smelt this ore is the blast furnace process, but the utilization rates of valuable components are low and the environment load is also serious. Some direct reduction processes have been adopted to use vanadium-titanium magnetite. Nevertheless, the reaction between carbon and phases containing Ti is slow, causing a high level of energy consumption and narrow range of operating temperature. Therefore, increasing attention has been paid to the gas-based direct reduction, and it seems to be a promising method to use HCVT.

The volumetric swelling of pellets during reduction significantly affects the stability and productivity of the shaft furnace production. The swelling mechanisms have been studied by many investigators. The growth of iron whiskers or fibrous iron has been the most widely accepted reason for the abnormal swelling. According to the results of their studies, the iron whisker or fibrous iron was formed at the formation stage of iron and severely destroyed the pellet structure. Other investigators also indicated that the growth of iron whiskers would be promoted by adding alkali. Many other factors were demonstrated to play important roles in the swelling behavior of iron ore pellets, such as the temperature, gas composition, reduction degree, pellets characteristics, etc. Hayashi and Iguchi comprehensively investigated the swelling of hematite pellets in H$_2$-CO gas mixtures and found that the swelling index initially increased and then decreased with increasing temperature. El-Geassy found that the rapid generation of H$_2$O and CO$_2$ caused an increase in the internal pressure such that the CO and H$_2$ levels significantly affected the swelling behavior. Additionally, many experts investigated the influence of gangue materials on the swelling behavior. Singh and Björkman found that the RSI increased with increasing levels of CaO, SiO$_2$, MgO, and Al$_2$O$_3$. Nonetheless, Sharma posited that these additives suppressed the growth of iron whiskers; then, the swelling index of the pellets would have a declining trend.

In summary, there are few reports on the swelling behavior of pellets during the gas-based direct reduction process, especially for HCVT pellets. Therefore, the swelling behavior of HCVT pellets...
during a reduction in the $\text{H}_2$-$\text{CO}$-$\text{CO}_2$ gas mixtures was studied, and the mechanisms were also deeply revealed.

**EXPERIMENTAL PROCEDURE**

**Raw Materials**

The green pellets, which were prepared from high-chromium, vanadium-titanium magnetite using a laboratory balling disc and contained 1 wt.% bentonite, were roasted for 20 min at 1573 K in air conditions. Then, the HCVT-oxidized pellets with an average diameter of 12.5 mm and crushing strength of 2878 N were obtained. The chemical compositions of the pellets (mass fraction, %) are TFe 59.4%, FeO 0.50%, Cr$_2$O$_3$ 0.589%, V$_2$O$_5$ 0.911%, TiO$_2$ 4.485%, Al$_2$O$_3$ 3.07%, SiO$_2$ 2.034%, MgO 1.03%, and CaO 0.21%. X-ray diffraction analysis was performed to determine the main phase containing Fe, Ti, V, and Cr. The results showed that Fe$_2$O$_3$ is the overwhelming phase in the oxidized pellets. Ti is presented in the form of Fe$_9$Ti$_{15}$O$_{48}$ and Fe$_2$Ti$_3$O$_9$; also, V and Cr generated their own solid solutions, Fe$_{0.7}$Cr$_{1.3}$O$_3$ and Cr$_{0.3}$V$_{1.7}$O$_3$.

**Method and Procedure**

The swelling behavior of the HCVT-oxidized pellets was studied in a laboratory gas-based shaft furnace, as shown in Fig. 1. First, the samples were placed into the effective zone of the furnace and heated to the target temperature in N$_2$ atmosphere. Then, the $\text{H}_2$-$\text{CO}$-$\text{CO}_2$ gas mixtures were introduced into the reactor with a flow rate of 4 L/min. The weight loss was captured by an electronic balance, and the reduction degree was evaluated as the fraction of oxygen removed from the iron oxides. The crucible was removed from the furnace and cooled in argon gas when the reduction was complete. Finally, the reduction swelling index (RSI) and compressive strength (CS) of the reduced samples were measured. The reduction temperature varied from 1223 K to 1273 K, to 1323 K to 1373 K, and the volume ratios of $\text{H}_2$/CO in the reducing gas were 2/5, 1/1, and 5/2. The concentration of CO$_2$ was kept constant at 5%.

The RSI of pellets during the reduction was calculated through Eq. 1:

$$\text{RSI} = \frac{V_0 - V_t}{V_0} \times 100\%$$

where $V_0$ and $V_t$ were the volumes of the samples before and at $t$ min of the reduction process, respectively, mm$^3$. The diameters of the oxidized pellets and reduced samples were all measured using a Vernier caliper.

**RESULTS AND DISCUSSION**

**Effects of Temperature on the RSI of HCVT Pellets**

The effects of temperature on the RSI of HCVT pellets are shown in Fig. 2. As presented in Fig. 2, the volume change of the pellets during reduction
can be divided into three stages. Initially, the pellets rapidly expand as a result of the fast reduction rate. Then, the expansion trend weakens after a turning point, and the RSI reaches the maximum slowly. Subsequently, the pellets begin to shrink. In Fig. 2a, as the temperature increased from 1223 K to 1373 K, the maximum RSI significantly increased from 14.68% to 22.54%, while the time for the pellets to reach the maximum RSI was shortened from 16 min to 6 min. The trends are similar in the atmosphere of H2/CO = 1/1 and 2/5. Therefore, it can be concluded that the RSI of HCVT pellets during reduction increases with increasing temperature.

Considering it is obvious that the trend of the second expansion stage also varied with temperature, the temperature mainly affects the swelling behavior of the pellets at this stage. Additionally, the results in Fig. 2d show that the RSI of HCVT pellets during reduction increases with increasing temperature.

Fig. 2. Effects of temperature on the RSI of HCVT pellets during reduction: (a) H2/CO = 5/2, (b) H2/CO = 1/1, (c) H2/CO = 2/5, and (d) reduction degree of the pellets with the maximum RSI at different temperatures.

Effects of Gas Composition on the RSI of HCVT Pellets

The volume change of HCVT pellets with different reducing gas ratios at 1223–1373 K is given in Fig. 4. As demonstrated in Fig. 4c, pellets in H2/CO = 5/2 reach a maximum RSI of 21.25% in 20 min
at the temperature of 1273 K. When the volume ratio of H₂/CO changed to 2/5, the maximum RSI slightly decreased by 8–19.55%. In other words, the RSI during reduction decreased with increasing H₂ content. Meanwhile, the expansion range also narrowed, and the peaks of the curves moved left, with an increasing ratio of H₂.

Figure 5 shows the microstructure analyzed by SEM–EDS and relative distribution of the phases-bearing Fe and Ti of pellets with a maximum RSI in H₂/CO = 1/1: (a) 1373 K, (b) 1323 K, (c) 1273 K, (d) 1223 K, (e) EDS analysis of phases of A to C, and (f) relative distribution of the phases-bearing Fe and Ti.

![Figure 5](image)

Fig. 3. SEM–EDS analyses and relative distribution of the phases-bearing Fe and Ti of pellets with a maximum RSI in H₂/CO = 1/1: (a) 1373 K, (b) 1323 K, (c) 1273 K, (d) 1223 K, (e) EDS analysis of phases of A to C, and (f) relative distribution of the phases-bearing Fe and Ti.

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It is also noted from Fig. 4 that the shrinking rate of the pellets in the late reduction stage increases with the content of H₂. The microstructure of the pellets with a reduction degree of 90% at different atmospheres was analyzed. As displayed in Fig. 6b, the iron phase precipitates in the form of an iron whisker. As a result of the different crystalline orientation of metallic iron, the growth of the iron whisker is disordered and fast, as well as pushed the surrounding grains loose, leading to severe destruction of pellet structure. Nonetheless, a dense iron phase formed in the pellets as a result of the different precipitation form of iron in the H₂-rich atmosphere, as observed in Fig. 6a. The softening deformation and aggregation caused the contraction of pellets.

Effects of the Reduction Degree on the RSI of HCVT Pellets

As mentioned previously, the volume change of the pellets during reduction can be divided into three stages, which exactly correspond to the three phase transition stages of iron oxide. The early stage is Fe₂O₃ → Fe₃O₄, which occurs at a reduction degree range of 0–20%. Because of fast phase transformation at the surface, the pellets rapidly expand in this stage. Then, Fe₃O₄ and Fe₂.₇₅Ti₀.₂₅O₄ → wüstite in the middle stage, and there is a reduction degree range of 20–50%. The expansion trend of the pellets weakens as a result of the slow reduction rate. Additionally, the pellets reach a maximum RSI when the reduction degree is approximately 35–50%. The final stage is wüstite → Fe, during which the pellets begin to contract because of the softening deformation and aggregation of the metallic iron.

It is noteworthy that the critical reduction degree of each expansion stage of HCVT pellets is larger than that of ordinary hematite pellets because of the complex phase composition and mineral structure of HCVT. Although the reaction quickly occurs at the surface, the reaction of the pellet core is slow. This causes an increase in the thermal stress, but the phase transformation is also later than that of ordinary hematite pellets.

The microphotographs of the pellets with different reduction degrees at 1373 K and H₂/CO = 5/2 are given in Fig. 7. Meanwhile, Table I shows the element proportions of the phases A through D. The compact structure of the oxidized pellets (as shown in Fig. 7a) is severely destroyed because of the transformation of hematite (point D) to magnetite (point A). When the reduction degree reaches 30%, some wüstite phase (point B) appears and the structure of the reduced pellets loosens, leading to a significant increase in the pellet RSI. As the reduction degree increased to 40%, massive wüstite was detected and further aggravated the damage to the pellets structure, which increased the RSI of pellets. As the reduction proceeded, the dominant phase of the pellets changed from wüstite into iron (point C) in the late stage of the reduction. The previously generated cracks and pores gradually decreased with the aggregation and growth of iron grains, resulting in the contraction of pellets.
Fig. 5. SEM–EDS analyses and relative distribution of the phases-bearing Fe and Ti of pellets with a maximum RSI at the temperature of 1273 K: (a) $H_2/CO = 5/2$, (b) $H_2/CO = 1/1$, (c) $H_2/CO = 2/5$, (d) EDS analysis of phases of A to C, and (e) relative distribution of the phases-bearing Fe and Ti.

Fig. 6. SEM images of pellets with a reduction degree of 90% at different atmosphere: (a) $H_2/CO = 5/2$ and (b) $H_2/CO = 2/5$. 
CONCLUSION

The effects of temperature, gas composition, and reduction degree on the swelling behavior of high-chromium, vanadium-bearing titanomagnetite pellets during the reduction in H$_2$-CO-CO$_2$ gas mixtures are examined. The main conclusions are summarized as follows:

1. The volume change of HCVT pellets during the reduction process can be divided into three stages. In the initial stage, the RSI of the pellets sharply increases. Then, there is a turning point, and the RSI reaches the maximum slowly. Afterward, the pellets begin to contract.

2. Temperature significantly affects the swelling behavior of HCVT pellets with the temperature range from 1223 K to 1373 K. The maximum RSI increased from 14.68% to 22.54% in H$_2$/CO = 5/2. Nevertheless, the expansion range was narrowed with the increasing temperature.

3. Pellets can quickly pass the wüstite generation stage in H$_2$-rich atmospheres and, consequently,

Table I. Element proportions of phases A through D

| A     | Fe | O  | Ti | V  | Cr | B     | Fe  | O  | Ti | V  | Cr | C     | Fe  | O  | Ti | V  | Cr | D     | Fe  | O  | Ti | V  | Cr | Fe  | O  | Ti | V  | Cr |
|-------|----|----|----|----|----|-------|----|----|----|----|----|-------|----|----|----|----|----|-------|----|----|----|----|----|----|----|----|----|----|
| Atomic ratio/| 39.4 | 56.9 | 2.8 | 0.5 | 0.4 | 42.9 | 47.4 | 8.9 | 0.4 | 0.4 | 50.7 | 47.2 | 2.1 | 95.6 | 4.4 |
| wt.%    | 64.1 | 30.3 | 4.1 | 0.8 | 0.7 | 68.2 | 21.6 | 9.0 | 0.6 | 0.6 | 77.5 | 20.7 | 1.8 | 98.6 | 1.4 |

Fig. 7. SEM–EDS analysis of pellets with different reduction degrees (1373 K, H$_2$/CO = 5/2): (a) 0%, (b) 13%, (c) 30%, (d) 40%, (e) 90%, and (f) EDS analysis of phases of A to D.
show a small RSI. Additionally, as the volume ratio of H₂/CO varied from 5/2 to 2/5 at 1273 K, the shrinking rate of the pellets decreased from 33.20% to 27.26% as a result of the formation of iron whiskers.

4. Massive wüstite was generated at the reduction degree range of 20–50% and caused most of the volume expansion. The RSI of HCVT pellets reached a maximum when the reduction degree was approximately 35–50%, which is theoretically located in the generation stage of wüstite.

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