Thermodynamic Analysis of the Reduction of Vanadium-titanium Magnetite by Gasification Gas

Wei-bin Chen, Zhaoqi Dong and Xi-dong Wang*

* Corresponding author. E-mail: xidong@pku.edu.cn

Received date: May 1, 2022
Accepted date: June 8, 2022
Advance published date: July 5, 2022

DOI: https://doi.org/10.2355/isijinternational.ISIJINT-2022-182

Please cite this article as:
https://doi.org/10.2355/isijinternational.ISIJINT-2022-182
Thermodynamic analysis of the reduction of vanadium-titanium magnetite by gasification gas

Wei-bin Chen\textsuperscript{a,b,c}, Zhaoqi Dong\textsuperscript{a,b,c} and Xi-dong Wang\textsuperscript{a,b,c}

\textsuperscript{a} Department of Energy and Resources Engineering, College of Engineering, Peking University, Beijing 100871, PR China.

\textsuperscript{b} School of Materials Science and Engineering, Peking University, Beijing 100871, PR China.

\textsuperscript{c} Beijing Key Laboratory for Solid Waste Utilization and Management, Peking University, Beijing, 100871, PR China

Wei-bin Chen: chenwb@pku.edu.cn;

Zhao-qi Dong: dongzhaoqi@pku.edu.cn

* Corresponding Author: Xi-dong Wang: xidong@pku.edu.cn
Abstract: Vanadium-titanium magnetite (VTM) has a high comprehensive utilization value. The gas-based reduction process combined with the electric furnace melting process has the advantages of a high recovery rate of precious metal elements in VTM, low cost, high-energy efficiency, and low environmental pollution. Gasification gas provided by coal gasification technology is a potential reducing agent. Through \textit{FACTSAGE} calculations and experiments, the reduction thermodynamic properties of VTM oxidized pellets by gasification gas were systematically studied to illustrate the feasibility of the system before practical experiments. The reaction mechanism of the direct reduction of VTM by gasification gas was proved, and the conversion behavior of iron and titanium in the reduction system was also clarified. This work clearly describes the reduction process of VTM oxidation pellets and clarifies the essence of the direct reduction of gas groups of VTM oxidized pellets.

Keywords: Vanadium-titanium magnetite; Gasification gas; Direct reduction; Thermodynamic analysis
1. Introduction

Vanadium-titanium magnetite (VTM) is a composite polymetallic ore composed of titanium (Ti), iron (Fe), and vanadium (V)\(^1\)-\(^2\). VTM is widely distributed in China, the United States and India\(^3\)-\(^4\). The key to using VTM is to effectively separate and extract the valuable metals, such as iron, vanadium, and titanium\(^5\). Currently, the blast furnace process is the primary technology for utilizing VTM\(^6\)-\(^7\). Because a solvent is introduced in this process, not only the grade of titanium in the blast furnace slag is very low, but TiO\(_2\) reacts with the solvent (CaO) to form perovskite, which makes it difficult to extract the titanium resources from VTM. More importantly, although the current blast furnace process dominates the global steel industry, it has obvious disadvantages. First, this process consumes a large amount of coke\(^8\), and the current lack of coke resources cannot support the long-term sustainable development of the blast furnace process. In addition, the blast furnace ironmaking process consumes a massive amount of energy and causes serious pollution\(^9\). Non-blast furnace processes, especially gas-based reduction processes\(^10\)-\(^11\), have great potential\(^12\)-\(^13\). The gas-based reduction process combined with the electric furnace melting process does not require the use of coke or the addition of calcium oxide and has the advantages of a high recovery rate of precious metal elements in iron ore, low-cost, high-energy efficiency, and low environmental pollution\(^14\)-\(^15\). Natural gas is currently the main gas-reducing agent used in the gas-based reduction process around the world\(^16\). However, China's natural gas reserves are insufficient, and resources are unevenly distributed\(^17\), which severely limits the development of China's gas-based reduction. Fortunately, China has abundant
As shown in Fig. S1 (Supporting Information), combining China's abundant coal resources and increasingly mature gasification technology, our research group proposed a new process for the integration of flue gas gasification and the direct reduction of VTM that opens an effective way to develop gas-based direct reduction technology. We conducted a feasibility study on the production of gasification gas from coal and biomass and found that the main components of gasification gas are carbon monoxide (CO) and hydrogen (H\textsubscript{2}). In this process, gasification gas was used as the reducing agent, and the flue gas after the VTM reduction was used as the gasification agent for coal gasification. The gas-based direct reduction of VTM does not add solvent and coal as the reducing agent, therefore, the product is relatively pure.

A thermodynamic analysis of the Gibbs free energy changes was conducted for a feasibility analysis of the system before practical experiments. Some key reactions of VTM reduction were carried out by this method, and our research group also conducted exploratory research. However, as a complex symbiotic mineral of iron, titanium, vanadium, and oxygen, the reaction process of VTM is very complex. Moreover, the effects of the reaction temperature, gasification gas flow rate, composition on the phase composition, and reduction degree of the product need to be further explored. Therefore, in this work, based on the analysis of FactSage software (www.factsage.com), a detailed thermodynamic study of the gas-based direct reduction of VTM was carried out. First, the phase composition and proportion of the VTM were determined by XRD, XRF, and XPS analyses. The effects of reduced temperature, total
amount of reducing gas, gasification gas composition, and reaction pressure on the direct reduction of VTM oxidized pellets were systematically studied. Furthermore, the reduction characteristics of the VTM were studied by VTM reduction experiments. The reduction degree and phase composition of the VTM were confirmed. In this work, the reaction mechanism of the gas-based direct reduction of VTM oxidized pellets was determined, and the transformation behavior of substance types in the system was also clarified.

2. Materials and methods

Materials
The VTM ore was obtained from Panzhihua, China. As shown in the XRD pattern of the VTM ore in Fig. 1, the main mineral phases of the VTM ore are titanomagnetite (TTM, the solid solution formed by magnetite as the main component and ilmenite spar) and ilmenite (FeTiO$_3$). The VTM oxidized pellets were prepared as we have described in our published paper 26). The VTM in the subsequent calculation simulations and experiments in this article refers to VTM oxidized pellets. The chemical compositions of VTM oxidized pellets are listed in Table 1. Fig. 1 indicates that TTH (the solid solution formed by hematite as the main component and ilmenite) and pseudobrookite (Fe$_2$TiO$_3$) are the main mineral phases in the VTM oxidized pellets. As shown in Fig. 2, the spatial feature is the close symbiosis of Fe$_2$O$_3$—TiO$_4$—MgO·Al$_2$O$_3$—FeO·TiO$_2$. Moreover, MgO and VO replace a part of the FeO, which greatly increases the difficulty of reduction.

Simulation Methods
FactSage is a commercially available software that was introduced in 2001 as the
fusion of the F*A*C*T/FACT-Win (Thermfact, Canada) and ChemSage (GTT-Technology, Germany) thermochemical packages. *FactSage (8.1 version)* uses the ChemSage Gibbs energy minimization routine and has been trusted and utilized by researchers in the field of materials and metallurgy\(^\text{27}\). The equilibrium compositions were calculated using the **Equilib** module of *FactSage*\(^\text{28}\) based on the conservation of mass and energy and minimization of the total Gibbs free energy. FactPS, FToxid and FTsalt of *FactSage* are selected for the simulated database. The amount of VTM is 200g, which is converted into molar amount and input into *FactSage*. The reducing gas takes the volume as the variable, which is also converted into the molar quantity and input into *FactSage*. The ratio between H\(_2\) and CO is volume ratio/molar ratio. In the experimental section, the reducing gas is continuously fed into the reactor at a given flow rate. We extended the reaction time to 240 min at a certain temperature to achieve a sufficient reaction. In the thermodynamic calculation section using *FactSage*, we convert the reducing gas flow to the total amount of reducing gas. We calculate the total amount of reducing agent by multiplying the reducing gas flow by 240 min. Then we use this calculated total amount of reducing gas as the input parameter of the *FactSage*, and the total amount of reducing gas in a single calculation is taken as the variable.

**Experimental Methods**

To investigate the direct reduction feasibility of VTM, reduction experiments were performed. As shown in Fig. 3, the experimental device consisted of a gasification gas flow control cabinet, tube furnace, refractory alloy steel material reactor, gas analyzer, electronic balance, and computer. The VTM oxidized pellets were evenly spread on the corundum balls. The tube furnace power was turned on, and the heating program was started. During the heating process, N\(_2\) was passed into the reactor as a protective gas.
The volume ratio of N\textsubscript{2} in reducing gas is 25%. At the specified temperature, the gasification gas was cut for reduction. During the reduction process, the electronic balance continuously recorded the weight loss of the pellet to obtain the reduction degree of the VTM. The gas analyzer continuously collected exhaust gas data. After the reduction, the N\textsubscript{2} was removed. In order to maintain the airtightness of the reaction system, we placed the thermocouple outside the tube during the reduction experiments. Therefore, before we carried out the reduction experiments, we carried out temperature calibration experiments to estimate the actual temperature of the sample through the thermocouple outside the furnace tube, and the experimental device is shown in Fig. S2.

**Characterization**

The patterns of X-ray diffraction (XRD) were collected by a powder X-ray diffractometer (Rigaku Dmax-2400, RIGAKU, Japan) with Cu K\textalpha radiation. Scanning electron microscopy (SEM) was performed on a field emission SU8010N instrument, operating at an accelerating voltage of 10 kV. The surface compositions and valence states of Ti and Fe in VTM were characterized by an X-ray photoelectron spectroscopy (AXIS Supra, Kratos Analytical Ltd, UK) with Al K\textalpha radiation.

**3. Results and discussion**

**3.1. Reactions of the VTM reduction system**

Owing to the low vanadium content of VTM in this raw material, thermodynamic research on the vanadium phase was not conducted in this work but has been reported in many previous studies\textsuperscript{14, 29-30}. Therefore, this work focuses on the iron and titanium phases in VTM. The reduction reaction of ordinary iron ore under CO or H\textsubscript{2}
atmospheres can be described by Eqs. (1)–(8), as shown in Table 2. Similarly, the most likely reaction in the VTM oxidized pellets in a reducing atmosphere of CO or H\(_2\) is described by Eqs. (9)–(18). The VTM reaction system should also include reactions of the gasification gas Eqs. (19)–(24). It can be seen that because of the close symbiosis of titanium and iron, the reduction of VTM is more complicated than that of ordinary iron ore.

Fig. S3 shows the \(\Delta_G^0\) of the main reaction in the VTM reduction system at 273-2073 K as a function of temperature. For most reactions, as the temperature increases, the Gibbs free energy decreases to less than zero. In the range of 400–1600 K, the \(\Delta_G^0\) of the reaction in Eq. (1) is smaller than that in Eq. (9). Therefore, in the range of 400–1600 K, under a CO atmosphere, Fe\(_2\)TiO\(_5\) is more difficult to be reduced than Fe\(_2\)O\(_3\).

In the reaction in Eq. (7), \(\Delta_G^0\) is smaller than in Eqs. (11), (13), (15), and (17). Therefore, Fe\(_2\)TiO\(_4\), FeTiO\(_3\), and FeTi\(_2\)O\(_4\) are more difficult to be reduced than FeO in the range of 400–1900 K, and VTM is more difficult to be reduced than the equivalent ordinary iron ore. In addition, the value of \(\Delta_G^0\) shown in Fig. S3 indicates that Fe\(_2\)TiO\(_5\) is more easily reduced in the VTM oxidation pellets than Fe\(_2\)TiO\(_4\).

Through thermodynamic calculations, the dominant regions and reduction curves of each phase in the VTM were plotted. Fig. 4 (a) shows the change in CO equilibrium concentration with temperature during the reduction of iron oxides, and Fig. 4 (b) shows the change in H\(_2\) equilibrium concentration with temperature during the iron
oxide reduction process. At the stage of FeO reduction to metallic iron, the equilibrium concentration of CO was approximately 72% at 1400 K, and the theoretical thermodynamic conversion of CO is approximately 28% at 1400 K, which is the case for ordinary iron concentrates. However, when the FeTiO$_3$ in VTM was reduced to metallic iron, the equilibrium concentration of CO increased sharply to 91% at 1400 K, the theoretical thermodynamic conversion rate of CO was only approximately 9% at 1400 K, and the maximum gas utilization rate was only approximately 6%. It is difficult to achieve thermodynamic equilibrium in the actual process, and the gas utilization rate will be lower. This leads to a lower efficiency in the reduction process and a significant increase in production costs. This is also the primary reason why VTM is more difficult to reduce than ordinary iron concentrates. The $\Delta_rG^\theta$ of VTM in 973 K -1373 K are shown in Table S1-S4.

3.2 Thermodynamic calculation: Effects of temperature on equilibrium compositions

First, we explored the effect of the reduction temperature. The other reaction conditions are listed in Table S5 and were fixed. We analyzed the equilibrium composition under the five reduction temperatures of 973, 1073, 1173, 1273, and 1373 K. The effect of the reduction temperature on the equilibrium yield of the solid compounds and gas, is shown in Table S6 and S7. Fig. 5 shows the effect of the reduction temperature on the composition of the equilibrium system. As the reduction temperature increased, the amount of metallic iron produced gradually increased. When the reduction temperature increased to 1373 K, the amount of metallic iron stabilized. In addition, the mass of the
residue decreased with increasing temperature. When the reduction temperature increased to 1373 K, the mass of the residue tended to stabilize. It should be noted here that when the reduction temperature was 973 K, some carbon was generated. When the reduction temperature increased to 1073 K, carbon was no longer generated. This is due to the reaction that generates carbon. Eqs. (19) and (21) represent an exothermic reaction, although the reaction to generate carbon from the cracking of CH$_4$ Eq. (23) is endothermic. However, the reaction Eq. (20) that generates CH$_4$ is exothermic. As the reduction temperature increased, the amount of CH$_4$ generated gradually decreased. Therefore, the reaction to generate carbon was suppressed as the reduction temperature increased.

When the reduction temperature was 973 K, a large amount of Fe$_2$TiO$_4$ was produced. At this temperature, MgTiO$_3$ reacted with FeO to form MgO and FeTiO$_3$. The generated MgO reacted with SiO$_2$ and Al$_2$O$_3$ to form Mg$_2$SiO$_4$ and Mg$_4$Al$_{10}$Si$_2$O$_{23}$. At the same time, the generated FeTiO$_3$ was converted into Fe$_2$TiO$_4$. On the one hand, Fe$_2$O$_3$ reduction takes precedence over FeTiO$_3$ reduction. The $\Delta_r G_0$ of the side reactions Eqs. (19), (21), (23), such as C and CH$_4$, is smaller than that of the FeTiO$_3$ reduction Eq. (15), resulting in FeTiO$_3$ not being reduced. On the other hand, the reduction of Fe$_2$O$_3$ was carried out in steps, and the $\Delta_r G_0$ of the side reactions Eqs. (19), (21), (23), such as C and CH$_4$, is also smaller than that of FeO reduction Eqs. (7) and (8), which led to a backlog of FeO. In addition, FeSiO$_3$ existed in the time-equilibrium product. When the reduction temperature rose to 1073 K, the degree of FeO backlog reduced, and
FeSiO$_3$ was no longer generated. More importantly, at this temperature, the $\Delta_r G_\theta$ of the Fe$_2$TiO$_4$ formation reaction is very small. This series of factors provided the conditions for the formation of Fe$_2$TiO$_4$. When the reduction temperature increased to 1073 K, the side reactions were suppressed. Not only was Fe$_2$TiO$_4$ not formed, but the FeTiO$_3$ was partially reduced. However, TiO$_2$ did not exist stably and reacted with MnO to form MnTiO$_3$. When the reduction temperature further increased to 1173 K, FeTiO$_3$ was completely reduced. When the reduction temperature increased to 1273 K, MgTi$_2$O$_5$ was generated. When the reduction temperature increased to 1373 K, Mg$_2$SiO$_4$ no longer formed, but the amount of MgTi$_2$O$_5$ increased. For vanadium, V$_2$O$_3$ could react with FeO to form FeV$_2$O$_4$ at low temperatures. As the reduction temperature increased, FeV$_2$O$_4$ no longer formed, and vanadium existed as V$_2$O$_3$. This is mainly because the reaction to form FeV$_2$O$_4$ is exothermic.

Fig. 5 also shows the effect of the reduction temperature on the equilibrium yield of the gaseous substances. Because the generation of CH$_4$ is an exothermic reaction, the mole fraction of CH$_4$ in the gas phase decreases with increasing temperature. When the temperature increased to 1273 K, the mole fraction of CH$_4$ was only 0.00006. When the reaction temperature was 973 K, even if some H$_2$O was generated, the mole fraction of H$_2$O was still less than that of CO$_2$. This shows that the reduction ability of CO is stronger than that of H$_2$ at 973 K. When the temperature increased to 1173 K, the mole fraction of H$_2$O was greater than that of CO$_2$, indicating that at this temperature, the reduction ability of H$_2$ is stronger than that of CO.
3.3 Thermodynamic calculation: Effects of the gasification gas flow rate on equilibrium compositions

We also explored the effect of the gasification gas flow. The other reaction conditions are listed in Table S8 and have been fixed. Fig. 6 shows the relationship between the gasification gas flow rate and the metal iron production, residue mass, and gas phase composition. The equilibrium production of metallic iron increases with the increase in gasification gas flow rate, until the flow rate reaches 5 L/min, after which the production amount tends to be stable. The mass of the residue decreases with the increase in gasification gas flow rate, until the reducing degree of the pellets becomes stable after the flow rate increases to 5 L/min. The effect of the gasification gas flow rate on the equilibrium production of solid compounds is also shown in Table S9. When the gasification gas flow rate is 2 L/min, MgTiO$_3$ is completely consumed. Because Fe$_2$O$_3$ is reduced to form FeO, and MgTiO$_3$ reacts with FeO to form MgO and FeTiO$_3$, the generated MgO reacts with SiO$_2$ and Al$_2$O$_3$ to form Mg$_2$SiO$_4$ and Mg$_4$Al$_{10}$Si$_2$O$_{23}$.

When the reduction temperature is 1273 K, the $\Delta G_0$ of the FeTiO$_3$ being reduced to TiO$_2$ is smaller than that of the FeTiO$_3$ being reduced to FeTi$_2$O$_5$. According to the $\Delta G_0$ of each reduction reaction of Fe$_2$O$_3$, it can be concluded that the reduction of Fe$_2$O$_3$ is not a one-step process but a step-by-step process. The specific process occurs because the $\Delta G_0$ of the Fe$_2$O$_3$ reduction to Fe$_3$O$_4$ is smaller than the $\Delta G_0$ of Fe. Fe$_2$O$_3$ is first reduced to Fe$_3$O$_4$. Then, Fe$_3$O$_4$ is reduced to FeO instead of Fe, and FeO is finally reduced to Fe. When the reduction temperature was 1273 K, whether H$_2$ or CO was
used as the reducing agent, the $\Delta rG^\theta$ at each stage of the $\text{Fe}_2\text{O}_3$ reduction was smaller than the $\Delta rG^\theta$ of $\text{FeTiO}_3$ reduction. Therefore, when the gasification gas flow was small and the gasification gas was insufficient, $\text{Fe}_2\text{O}_3$ was preferentially reduced. When the gasification gas flow was increased to 3 L/min, a small amount of $\text{FeTiO}_3$ was reduced to obtain $\text{TiO}_2$ and Fe. However, $\text{TiO}_2$ does not exist stably but reacts with MnO to form $\text{MnTiO}_3$. This is because the $\Delta rG^\theta$ of $\text{TiO}_2$ reacting with MnO is less than zero, and the reaction occurs easily. When the flow of gasification gas was increased to 4 L/min, FeTiO$_3$ was completely reduced, and the amount of $\text{TiO}_2$ increased. MgTi$_2$O$_5$ and TiO$_2$ were formed in the equilibrium product. Because the $\Delta rG^\theta$ of MnTiO$_3$ was less than that of MgTi$_2$O$_5$, MnTiO$_3$ preferentially formed. When the flow of the gasification gas was small, the $\text{V}_2\text{O}_3$ reacted with FeO to form FeV$_2$O$_4$. As the flow of gasification gas increased, FeV$_2$O$_4$ was no longer generated.

3.4 Thermodynamic calculation: Effects of the gasification gas composition on equilibrium compositions

We also explored the effect of the gasification gas composition at gas flow rates of 3L/min and 5L/min, respectively. The reaction conditions are listed in Table S10. This work analyzes the effect of the gasification gas carbon-hydrogen ratio ($n(\text{CO})/n(\text{H}_2)$) on the VTM reduction equilibrium system, under the conditions of gasification gas flows of 3 L/min and 5 L/min.

When the gasification gas flow rate is 5 L/min, the effect of the carbon-hydrogen ratio (the ratio of the moles of CO to the moles of H$_2$ in the gasification gas, $n(\text{CO})/n(\text{H}_2)$)
on the equilibrium production of iron and the composition of the solid phase material are shown in Table S11. When the gasification gas flow rate was 5 L/min, with the gasification gas carbon-hydrogen ratio changing, there was no change in the amount of iron produced. This phenomenon indicates that when the flow rate is 5 L/min, the gasification gas is sufficient. Similar to the results of studies by Jeongseog 31), under the condition that the gasification gas is sufficient, the difference between the reducing capacities of H\(_2\) and CO is not the influencing factor in the reduction reaction; the carbon-hydrogen ratio has no detailed effect on the reaction.

Therefore, we reduced the gasification gas flow rate under the calculation conditions to 3 L/min. Fig. 7 shows the effect of the carbon-hydrogen ratio on the composition of the equilibrium system. As the carbon-hydrogen ratio increases, the equilibrium production of metallic iron decreases. This is because H\(_2\) has a stronger reducing ability than CO when the reduction temperature is 1273 K. The effect of changes in the carbon-hydrogen ratio on the equilibrium yield of solid compounds when the gasification gas flow rate was 3 L/min is shown in Table S12. FeTiO\(_3\) cannot be completely reduced when the H\(_2\) content in the gasification gas is low. As the H\(_2\) content increased, more FeTiO\(_3\) was reduced. Therefore, to enhance the reducing ability of the gasification gas, the carbon-hydrogen ratio should be reduced as much as possible, that is, the H\(_2\) content should be increased.

We investigated the influence of reaction pressure (1-6 atm) on the reaction system.
The reaction conditions are listed in Table S13. The effects of the reaction pressure on the equilibrium compositions of the solid compounds and gas products are shown in Tables S14 and S15. The reaction pressure has almost no effect on the equilibrium production of iron and the quality of the residue. This is because, whether H$_2$ or CO is used as the reducing agent, Fe$_2$O$_3$ and FeTiO$_3$ reduction reactions are all equal volume reactions; therefore, the reaction pressure does not affect the equilibrium of the reaction.

3.5 Experimental analysis

3.5.1 Effects of temperature on the composition of reaction products and reduction degree

Fig. 8 (a) shows the final reduction degree and iron-containing product composition for reducing VTM oxidized pellets at different temperatures for 240 min, and the experimental conditions are shown in Table S16. Fig. 8 (b) is the XRD spectrum of the reduced product. As the reduction temperature increases, the final reduction degree of VTM continues to increase. When the reduction temperature reaches 1273 K, the final reduction degree of VTM tends to be stable, which is consistent with the thermodynamic calculation results. The phase of the reduced product also changes at different temperatures. For example, the main mineral phases at lower temperatures are Fe$_3$O$_4$ and Fe$_2$TiO$_4$. As the temperature increases, the content of FeO increases. The FeO step is reduced to Fe, and the FeTi$_2$O$_4$ exists stably. When the temperature reaches 1073 K, Fe$_2$TiO$_4$ is reduced to FeTiO$_3$. As the temperature further increases to 1173 K, the FeTiO$_3$ phase disappears, and the main mineral phases
of the reduction product are Fe and FeTi$_2$O$_5$. With increasing temperature, the content
of FeTi$_2$O$_5$ gradually decreases, which is consistent with the reaction path of the
thermodynamic analysis of Fig. 4. Based on these experimental results, it can be
concluded that a high temperature is beneficial for the reduction of VTM oxidized
pellets. Based on this, we recommend that the reduction temperature of VTM oxidized
pellets is set to 1273–1373 K in actual industrial production. The photos of the VTM
metalized pellets after reduction from 973 K to 1373 K are shown in Figs. 9 (a–e). As
can be seen from Fig. 9 (a), when the reduction temperature is 973 K, the outer surface
of the VTM metalized pellets is heavily wrapped in black powder. As can be seen from
Fig. 9 (b), when the reduction temperature increases to 1073 K, the amount of black
powder generated is reduced but still exists. When the reduction temperature increases
to 1173 K, the black powder is no longer generated and is not tightly adhered to the
surface of the pellets. The XRD pattern of the powder is shown in Fig. 9 (f), and carbon
was found in the black powder. The carbonation reaction occurred at the reduction
temperatures of 973 and 1073 K. The result of the simulation calculation is that carbon
is generated only at the reduction temperature of 973 K. There are some discrepancies
with the experimental research results, which may be because the reactor used in the
actual reduction is made of steel. Steel has a catalytic effect on the carbon precipitation
reaction. It was further verified that the reduction reaction is carried out progressively
from the outer layer of the pellet to the core. The uneven reduction rate in each layer of
the pellet causes stress in the pellet. As the reduction temperature increases, the
reduction rate is accelerated, and the difference between the reduction rate of the outer
layer of the pellet and that of the core increases. The resulting stress is enhanced; therefore, as the reduction temperature increases, the cracks in the VTM metalized pellets increase and become deeper. At the same time, as the reduction temperature increases, the density of the VTM metal pellets decreases, and the structure becomes increasingly looser. When the reduction temperature is 1373 K, the shell of the VTM metalized pellets begins to show obvious flaking.

**Fig. 10** shows the morphology of the VTM metalized pellets at the reduction temperature of 973–1373 K. As the reduction temperature increases, the VTM metalized pellets gradually exhibit a metallic luster. It can be seen from **Fig. 10** that when the reduction temperature is 973 K, the metallic iron crystals in the reduced VTM pellets gradually precipitate as a sheet-like structure, and the metallic iron wafers overlap each other with a certain degree of crystalline connection. When the reduction temperature rises to 1073 K, the metallic iron precipitates as fibrous iron whiskers. When the reduction temperature is increased to 1173 K, more metallic iron crystals are precipitated, which causes the fibrous metallic iron whiskers to fuse with each other, and the fibrous iron whisker structure disappears. When the reduction temperature is increased to 1273 K, the VTM metalized pellets have softened to a certain extent. When the reduction temperature is increased to 1373 K, the metallic iron aggregates in the metallization of the VTM and exhibits a granular structure, and the connection between the grains is weak.
3.5.2 Effects of the flow of gas on the composition of reaction products and reduction degree

Fig. 11 (a) shows the phase changes and final degree of reduction in the VTM reduction process at different gasification gas flows, and the experimental conditions are shown in Table S17. It can be seen from the figure that as the gasification gas flow increases, the final reduction degree of VTM increases. When the gasification gas flow rate increased to 5 L/min, the degree of reduction became stable. The thermodynamic calculation results showed that the reduction degree stabilized after the gasification gas flow rate reached 4 L/min. The difference is because the reduction process is also affected by kinetics. Fig. 11 (b) shows the XRD pattern of the VTM reduction products. FeTiO$_3$ is present in the VTM metalized pellets when the gasification gas flow rate is 2 L/min and 3 L/min, and the gasification gas flow continues to increase.

3.5.3 Effects of the gasification gas composition on the composition of reaction products and reduction degree

As with the thermodynamic calculations, we explored the effect of the carbon-hydrogen ratio of the gasification gas when the flow rate of the gasification gas was 3 L/min and 5 L/min. When the reaction gas flow rate was 5 L/min, the reduction degree of VTM oxidized pellets was not affected by the carbon-hydrogen ratio, which was consistent with the results of thermodynamic calculations.

Fig. 12 (a) shows the effect of the carbon-hydrogen ratio of the gasification gas on the phase composition and the final degree of reduction of the VTM oxidized pellet.
reduction system at a flow rate of 3 L/min, and the experimental conditions are shown in Table S18. The final reduction degree of the pellets indicates that the reducing ability of H₂ is stronger than that of CO, which is also consistent with the results of the thermodynamic calculations. Fig. 12 (b) shows the XRD pattern of the VTM oxidized pellets reduced by gasification gas with different gasification gas carbon-hydrogen ratios when the gasification gas flow rate was 3 L/min. It can be seen from the figure that when the carbon-hydrogen ratio is relatively large, titanium in the VTM metalized pellets exists in the form of FeTiO₃; when the carbon-hydrogen ratio is reduced to 2:1, FeTiO₃ is reduced to form FeTi₂O₅, which is consistent with the results of the thermodynamic calculations of Fig. 4.

3.5.4 Dynamic study of the reduction process by XPS

At 1273 K, the dynamic process of the reduction of VTM oxide pellets was verified by XPS at different reaction times. The flow rate of the gasification gas was 5 L/min, the carbon-hydrogen ratio was 1:1, and the diameter of the VTM oxidized pellets was 10–12 mm. The following six samples were subjected to XPS testing: VTM oxidized pellets, VTM oxidized pellets reduced for 10 min, VTM oxidized pellets reduced for 50 min, VTM oxidized pellets reduced for 90 min, and VTM oxidized pellets completely reduced (240min). In this way, the valence changes of Fe and Ti during the reduction of vanadium-titanium magnetite oxide pellets were explored.

Fig. 13 show the valence state distribution of Fe on the VTM (Fig. 13 (a)) and oxidized VTM (Fig. 13(b)), which are reduced by gasification gas for different time (10 min
(Fig. 13(c))\ 50 min \ (Fig. 13(d))\ 90 min \ (Fig. 13(e))\ 240 min \ (Fig. 13(f)), and the results of peak fitting. According to the electronic binding energy comparison table of Fe, the electron binding energy of the 2p$_{3/2}$ orbitals of Fe$^{2+}$ is approximately 710 eV, and the electron binding energy of the 2p$_{3/2}$ orbitals of Fe$^{3+}$ is approximately 713 eV. The relative concentration of Fe$^{2+}$ on the surface of the raw material was higher than that of Fe$^{3+}$, and the Fe$^{2+}$/Fe$^{3+}$ ratio was approximately 1.93 (Table 3). After oxidation, the relative content of Fe$^{3+}$ increased significantly, and the Fe$^{2+}$/Fe$^{3+}$ ratio decreased to 0.77, which also conformed to the distribution law of oxidized Fe valence. As the reduction reaction progressed, the Fe$^{2+}$/Fe$^{3+}$ ratio gradually increased, the relative content of Fe$^{2+}$ continued to increase, and the relative content of Fe$^{3+}$ continued to decline. During this process, the VTM was gradually reduced to elemental iron. Fig. 14 show the valence state distribution of Ti on the VTM (Fig. 14 (a)) and oxidized VTM (Fig. 14(b)), which are reduced by gasification gas for different times (10 min \ (Fig. 14(c))\ 50 min \ (Fig. 14(d))\ 90 min \ (Fig. 14(e))\ 240 min \ (Fig. 14(f)), and the results of peak fitting. According to the electronic binding energy comparison table of Ti, the electronic binding energy of the 2p$_{3/2}$ orbital of Ti$^{4+}$ is approximately 458 eV. It can be seen from the figure that the fine Ti spectrum of the raw material has more noise signals. That is because the relative content of the Ti element on the surface is low; therefore, the detected signal intensity is very low, and as the reduction reaction proceeds, the Ti fine spectrum is shown as a single peak (there is a slight interference from the O$_2$ spectrum at 459 eV), and the Ti element always exists in the form of Ti$^{4+}$ on the surface, which is consistent with the results of the thermodynamic calculations. During the
entire reduction process, the Ti$^{4+}$ oxides are always stable.

Table 3 shows the relative concentrations of Fe and Ti on the surface of each sample during the reduction process. The surface of the raw VTM was covered with more impurities. The relative concentration of Fe was very low, while Ti was present. After VTM was sintered by oxidation, the relative concentrations of Fe and Ti on the surface increased significantly. During the reduction of the VTM, as the reduction time increased, the concentration of Fe on the surface gradually decreased. This is due to the continuous progress of the reduction reaction, and the iron oxide in the VTM was gradually reduced to metallic iron. Therefore, the relative concentration of Fe on the surface decreased. In the process of the reduction reaction, the relative concentration of the Ti element decreased first and then increased. This can be understood in that when the Fe element was partially reduced, Ti remained in the eutectic structure with Fe, and the relative concentration of Ti gradually decreased. When the Fe was reduced to a certain extent, the Ti element broke away from the eutectic structure with Fe, and the relative concentration of Ti on the surface increased significantly.

4. Conclusions

Non-blast furnace processes, especially gas-based reduction processes have great potential. The integration of coal gasification and the direct reduction of VTM that opens an effective way to develop gas-based direct reduction technology. In this process, gasification gas was used as the reducing agent. In this work, the direct reduction of
VTM oxidized pellets by the gasification gas was systematically analyzed through experimental research and thermodynamic calculations.

(1) We give all possible reactions of the system in which VTM is reduced by gasification gas and the corresponding $\Delta_r G_0$.

(2) VTM oxidized pellets are more difficult to reduce, and the reduction process is more complicated. The reduction process of VTM oxidized pellets are clearly described.

(3) With an increase in the reduction temperature, the reduction degree of VTM oxidized pellets increases gradually, and the reduction system approaches equilibrium when the reduction temperature rises to 1273 K.

(4) This study lays a theoretical foundation for the integration of flue gas gasification and the direct reduction of VTM. The reduction temperature should be approximately 1273–1373 K, steam should be used for coal gasification as much as possible to obtain hydrogen-rich gasification gas.
Supporting Information

This material is available on the Journal website at https://doi.org/10.2355/isijinternational.ISIJINT-20XX-XXX.

Acknowledgements

This research was funded by the National Key Research and Development Plan of China (2018YFC1901503 and 2018YFC1901505), Shanxi Unveiling Bidding Project (20191101007), National Natural Science Foundation of China (51672006), and the Ministry of Land and Resources Public Welfare Industry Research Project (201511062-02).
References

https://doi.org/10.1080/03019233.2020.1721955

https://doi.org/10.2355/isijinternational.ISIJINT-2017-515

3) W. Zhao, M. Chu, H. Guo, Z. Liu, B. Yan, P Li: ISIJ Int., 61(2021), 146.
https://doi.org/10.2355/isijinternational.ISIJINT-2020-309

https://doi.org/10.1007/s11663-019-01756-0


https://doi.org/10.2355/isijinternational.ISIJINT-2020-004

https://doi.org/10.2355/isijinternational.ISIJINT-2018-175

https://doi.org/10.1016/j.mineng.2013.11.002

https://doi.org/10.1007/s10973-018-7687-8

https://doi.org/10.1080/03019233.2015.1104072

https://doi.org/10.1007/s12613-015-1123-x
https://doi.org/10.1007/s11663-016-0644-7

https://doi.org/10.1007/s12613-016-1331-z

https://doi.org/10.1007/s12613-019-1795-8

15) D. Wang, J. Xu, K. Ma, Y. Xu, J. Dang, M. Kou, X. Lv, L. Wen: Int J Hydrogen Energ,

https://doi.org/10.2355/isijinternational.ISIJINT-2020-303

https://doi.org/10.1016/j.jnggs.2020.07.004

https://doi.org/10.1016/j.jclepro.2019.119487

https://doi.org/10.3390/en12030496

1144. https://doi.org/10.1080/15435075.2019.1653881

https://doi.org/10.1016/j.energy.2018.11.019

https://doi.org/10.1016/j.energy.2018.02.119


List of Table and Figure Captions

**Table 1** Composition of VTM oxidized pellet, mass %

**Table 2** Reduction reaction equation in the reduction system of VTM

**Table 3** Changes in the concentrations of Fe and Ti in VTM during the reduction process

**Fig. 1** XRD patterns of VTM ore and VTM oxidized pellets

**Fig. 2** Schematic diagram of the lattice transformation of the main phases during the VTM oxidation roasting process: a(TTM); b(TTH); c(FeTiO₃); d(Fe₂TiO₅)

**Fig. 3** Schematic diagram of the experimental apparatus

**Fig. 4** Relationship between the equilibrium concentration of the gasification gas and temperature during the reduction of VTM in (a) CO; and (b) H₂

**Fig. 5** Effects of temperature on equilibrium compositions

**Fig. 6** Effects of gasification gas flow on equilibrium compositions

**Fig. 7** Effects of gasification gas composition on equilibrium compositions

**Fig. 8** Reduction of VTM oxide pellets at different temperatures for 240 min (a) Final reduction degree and product composition; (b) XRD pattern

**Fig. 9** (a-e) Photos of VTM metalized pellets at 973 K, 1073 K, 1173 K, 1273 K, and 1373 K; (f) XRD patterns of black powder products at 973 K (red line), and 1073 K (blank line)

**Fig. 10** SEM image of VTM metallized pellets (a) 973 K; (b) 1073 K; (c) 1173 K; (d) 1273 K; (e) 1373 K

**Fig. 11** Reduction of VTM pellets under different gasification gas flows for 240 min (a) Final reduction degree and iron-containing product composition; (b) XRD pattern

**Fig. 12** Reduction of VTM pellets under different gasification gas composition for 240 minutes (a) Final reduction degree and iron-containing product composition; (b) XRD pattern

**Fig. 13** XPS pattern of Fe in (a) raw materials of VTM; (b) oxidized VTM; the oxidized pellets are reduced by gasification gas for (c) 10 min; (d) 50 min; (e) 90 min; and (f) 300 min

**Fig. 14** XPS pattern of Ti in (a) raw materials of VTM; (b) oxidized VTM; the oxidized pellets are reduced by gasification gas for (c) 10 min; (d) 50 min; (e) 90 min; and (f) 300 min
Table 1 Composition of VTM oxidized pellet, mass %

<table>
<thead>
<tr>
<th></th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>V$_2$O$_5$</th>
<th>MnO</th>
<th>K$_2$O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass %</td>
<td>65.0</td>
<td>13.4</td>
<td>8.42</td>
<td>6.54</td>
<td>3.28</td>
<td>1.40</td>
<td>0.633</td>
<td>0.54</td>
<td>0.32</td>
<td>0.063</td>
<td>0.037</td>
</tr>
</tbody>
</table>
Table 2 Reduction reaction equation in the reduction system of VTM

<table>
<thead>
<tr>
<th>NO.</th>
<th>Reaction equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_3\text{O}_4 + \text{CO}_2$</td>
</tr>
<tr>
<td>2</td>
<td>$3\text{Fe}_2\text{O}_3 + \text{H}_2 = 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2$</td>
</tr>
<tr>
<td>4</td>
<td>$\text{Fe}_3\text{O}_4 + \text{H}_2 = 3\text{FeO} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>5</td>
<td>$1/4\text{Fe}_3\text{O}_4 + \text{CO} = 3/4\text{Fe} + \text{CO}_2$</td>
</tr>
<tr>
<td>6</td>
<td>$1/4\text{Fe}_3\text{O}_4 + \text{H}_2 = 3/4\text{Fe} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>7</td>
<td>$\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$</td>
</tr>
<tr>
<td>8</td>
<td>$\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>9</td>
<td>$\text{Fe}_2\text{TiO}_5 + \text{CO} = \text{Fe}_2\text{TiO}_4 + \text{CO}_2$</td>
</tr>
<tr>
<td>10</td>
<td>$\text{Fe}_2\text{TiO}_5 + \text{H}_2 = \text{Fe}_2\text{TiO}_4 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>11</td>
<td>$\text{Fe}_2\text{TiO}_4 + \text{CO} = \text{FeTiO}_3 + \text{Fe} + \text{CO}_2$</td>
</tr>
<tr>
<td>12</td>
<td>$\text{Fe}_2\text{TiO}_4 + \text{H}_2 = \text{FeTiO}_3 + \text{Fe} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>13</td>
<td>$2\text{FeTiO}_3 + \text{CO} = \text{FeTi}_2\text{O}_5 + \text{Fe} + \text{CO}_2$</td>
</tr>
<tr>
<td>14</td>
<td>$2\text{FeTiO}_3 + \text{H}_2 = \text{FeTi}_2\text{O}_5 + \text{Fe} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>15</td>
<td>$\text{FeTiO}_3 + \text{CO} = \text{TiO}_2 + \text{Fe} + \text{CO}_2$</td>
</tr>
<tr>
<td>16</td>
<td>$\text{FeTiO}_3 + \text{H}_2 = \text{TiO}_2 + \text{Fe} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>17</td>
<td>$3/5\text{FeTi}_2\text{O}_5 + \text{CO} = 2/5\text{Ti}_3\text{O}_5 + 3/5\text{Fe} + \text{CO}_2$</td>
</tr>
<tr>
<td>18</td>
<td>$3/5\text{FeTi}_2\text{O}_5 + \text{H}_2 = 2/5\text{Ti}_3\text{O}_5 + 3/5\text{Fe} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>19</td>
<td>$2\text{CO} = \text{CO}_2 + \text{C}$</td>
</tr>
<tr>
<td>20</td>
<td>$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>21</td>
<td>$\text{CO} + \text{H}_2 = \text{C} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>22</td>
<td>$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$</td>
</tr>
<tr>
<td>23</td>
<td>$\text{CH}_4 = \text{C} + 2\text{H}_2$</td>
</tr>
<tr>
<td>24</td>
<td>$\text{CH}_4 + 3\text{CO}_2 = 4\text{CO} (g) + 2\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>
Table 3 Changes in the concentrations of Fe and Ti in VTM during the reduction process

<table>
<thead>
<tr>
<th>Samples</th>
<th>Relative concentration of elements /%</th>
<th>Valence distribution of Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Ti</td>
</tr>
<tr>
<td>VTM</td>
<td>0.85</td>
<td>0</td>
</tr>
<tr>
<td>VTM oxidized pellets</td>
<td>6.15</td>
<td>3.45</td>
</tr>
<tr>
<td>10 min reduced</td>
<td>5.16</td>
<td>3.14</td>
</tr>
<tr>
<td>50 min reduced</td>
<td>4.49</td>
<td>2.08</td>
</tr>
<tr>
<td>90 min reduced</td>
<td>3.46</td>
<td>5.20</td>
</tr>
<tr>
<td>Complete reduction</td>
<td>1.13</td>
<td>5.60</td>
</tr>
</tbody>
</table>
Fig. 1 XRD patterns of VTM ore and VTM oxidized pellets
Fig. 2 Schematic diagram of the lattice transformation of the main phases during the VTM oxidation roasting process: a(TTM); b(TTH); c(FeTiO₃); d(Fe₂TiO₅)
Fig. 3 Schematic diagram of the experimental apparatus
(1-gas cylinder, 2-flow control cabinet, 3-gas mixing chamber, 4-reactor, 5-fever zone, 6-alundum tube, 7-corundum ball, 8-oxidized VTM pellets, 9- thermocouple, 10-tube furnace, 11-temperature controlling cabinet, 12-wash bottle, 13-drying bottle, 14-coal gas analyzer, 15-electronic balance, 16-computer.)
Fig. 4 Relationship between the equilibrium concentration of the gasification gas and temperature during the reduction of VTM in (a) CO; and (b) H₂
Fig. 5 Effects of temperature on equilibrium compositions. The x-axis is the reaction temperature (K). The blue y-axis on the left side of the figure represents mass of residual solids (sample input for VTM is 200 g) when the reaction reaches equilibrium, and the unit is g. The black/red y-axis on the left side of the figure represent the mol amount of Fe/C produced. The green/purple/yellow/cyan/grey y-axis on the right side of the figure represent the mole fraction of H$_2$O/CO$_2$/CO/H$_2$/CH$_4$ in the gas phase when the reaction reaches equilibrium. There is also a N$_2$ component in the gas phase with a mole fraction of about 0.25, which is introduced to be consistent with the experimental process and is not shown in the figure.
**Fig. 6** Effects of gasification gas flow on equilibrium compositions. The red y-axis on the left side of the figure represents mass of residual solids (sample input for VTM is 200 g) when the reaction reaches equilibrium, and the unit is g. The black y-axis on the left side of the figure represents the mol amount of Fe, and the unit is mol. The green/purple/yellow/cyan y-axis on the right side of the figure represent the mole fraction of H₂O/CO₂/CO/H₂ in the gas phase when the reaction reaches equilibrium. There is also a N₂ component in the gas phase with a mole fraction of about 0.25, which is introduced to be consistent with the experimental process and is not shown in the figure.
Fig. 7 Effects of gasification gas composition on equilibrium compositions. The blud y-axis on the left side of the figure represents mass of residual solids (sample input for VTM is 200 g) when the reaction reaches equilibrium, and the unit is g. The black y-axis on the left side of the figure represents the mol amount of Fe, and the unit is mol. The green/purple/yellow/cyan y-axis on the right side of the figure represent the mole fraction of H₂O/CO₂/CO/H₂ in the gas phase when the reaction reaches equilibrium. There is also a N₂ component in the gas phase with a mole fraction of about 0.25, which is introduced to be consistent with the experimental process and is not shown in the figure.
Fig. 8 Reduction of VTM oxide pellets at different temperatures for 240 min

(a) Final reduction degree and product composition; (b) XRD pattern
Fig. 9 (a-e) Photos of VTM metalized pellets at 973 K, 1073 K, 1173 K, 1273 K, and 1373 K, (f) XRD patterns of black powder products at 973 K (red line), and 1073 K (blank line)
Fig. 10 SEM image of VTM metallized pellets

(a) 973 K; (b) 1073 K; (c) 1173 K; (d) 1273 K; (e) 1373 K
Fig. 11 Reduction of VTM pellets under different gasification gas flows for 240 min

(a) Final reduction degree and iron-containing product composition; (b) XRD pattern
Fig. 12 Reduction of VTM pellets under different gasification gas composition for 240 minutes

(a) Final reduction degree and iron-containing product composition; (b) XRD pattern
Fig. 13 XPS pattern of Fe in (a) raw materials of VTM; (b) oxidized VTM; the oxidized pellets are reduced by gasification gas for (c) 10 min; (d) 50 min; (e) 90 min; and (f) 240 min
Fig. 14 XPS pattern of Ti in (a) raw materials of VTM; (b) oxidized VTM; the oxidized pellets are reduced by gasification gas for (c) 10 min; (d) 50 min; (e) 90 min; and (f) 240 min.
Graphical Abstract