Kinetics of Smelting Chromia–Bearing Vanadiferous Titanomagnetite Ore via High–Temperature CO2–Containing Gas Injection

Hanlin Song 1,2,3,4, Gongjin Cheng 1,2,3,4, Jianxing Liu 1,2,3,4, Jinpeng Zhang 1,2,3,4 and Xiangxin Xue 1,2,3,4,*

School of Metallurgy, Northeastern University, Shenyang 110819, China; 1710496@stu.neu.edu.cn (H.S.); chenggi@smm.neu.edu.cn (G.C.); liujianxing@smm.neu.edu.cn (J.L.); 1801576@stu.neu.edu.cn (J.Z.)
Liaoning Key Laboratory of Recycling Science for Metallurgical Resources, Shenyang 110819, China
Innovation Research Institute of Vanadium and Titanium Resource Industry Technology, Northeastern University, Shenyang 110819, China
Innovation Research Institute of Comprehensive Utilization Technology for Vanadium–Titanium Magnetite Resources in Liaoxi District, Chaoyang 122000, China
* Correspondence: xuexx@mail.neu.edu.cn

Abstract: Through thermodynamic smelting experiments, nonisothermal and isothermal kinetics experiments, the effects of CO2–containing gas injection on the smelting of chromia–bearing vanadiferous titanomagnetite ore were investigated. The experiments at 900 °C, 1000 °C, 1100 °C, 1200 °C, and 1300 °C, and CO2 concentration of 0, 10 vol.%, 20 vol.%, and 30 vol.% were studied. The samples after the kinetics experiments were analyzed through thermodynamic calculations and characterized by XRD, XRF, XPS, and SEM. The results of thermodynamic experiments show that the injection of CO2–containing gas significantly improves the softening–melting–dripping behavior during the smelting process. As the concentration of injected CO2 increased from 0 vol.% to 30 vol.%, the range of softening temperature [T40–T4] decreased from 109 °C to 97 °C, and the range of droplet temperature [T3–T4] decreased rapidly from 196 °C to 162 °C. Moreover, when CO2 concentration was 20 vol.%, the minimum apparent activation energy of nonisothermal kinetics reached 75.58 kJ mol⁻¹. Combining the lowest permeability index and the fastest nonsmooth reduction rate, the optimal CO2 concentration in the fuel gas was considered to be 20 vol.%. The isothermal parameters were fitted according to 1 − (1 − α)¹⁄³ − t (CG model), and the apparent activation energy was 121.93 kJ mol⁻¹ (less than 150 kJ mol⁻¹), which means that the restrictive step of the polynmetallic reaction is mainly determined by diffusion. Finally, thermodynamic calculations and characterizations show that CO2–containing gas injection helps titanium stabilize in a higher valence state, which is conducive to improve the high–temperature characteristics of titanium–containing slag.

Keywords: kinetics; ironmaking; CO2–containing gas; chromia–bearing vanadiferous titanomagnetite ore; apparent activation energy

1. Introduction

Chromia–bearing vanadiferous titanomagnetite ore (CVTO), as a special polymetallic resource, contains iron, vanadia, and titania, and has also associated chromia resources and therefore a high comprehensive utilization value. A blast furnace process for the comprehensive utilization of chromia–bearing vanadiferous titanomagnetite ore based on pyrometallurgy separation has been systematically established in China [1,2]. Hot air injection and oxygen–enriched air injection are common blowing methods in blast furnaces. However, due to the special nature of CVTO blast furnace smelting, under the combined action of coke and nitrogen in the injected air, the titanium dioxide in the samples is easily over–reduced to high melting point titanium carbonitride, which will cause the viscosity of the molten slag to increase sharply, even slag bubbling, difficulty in separating slag and iron that seriously endanger blast furnace production [3–6]. Moreover, the high furnace...
temperature caused by oxygen–enriched air injection is strictly not conducive to suppressing the production of titanium carbonitride, but it will also lead to a substantial increase in fuel consumption such as coke and coal powder. In addition, with the establishment of the international treaties for peak carbon dioxide emissions and carbon neutrality, low–carbon metallurgy is imperative [7–11]. Therefore, the reuse of high–temperature CO$_2$–containing gas (HCG) injection to replace part of the hot air injection was studied [2,11,12].

For the smelting behavior of the CVTO blast furnace with CO$_2$ injection, the corresponding kinetic research is rarely carried out. However, for a single reduction or oxidation of VTM powders or pellets or sinters, many kinetics studies have been carried out, but in terms of the calculation methods of the reduction rate, the kinetics models, the activation energy, and the criteria for limitations are quite different [13–20]. More importantly, pellets and sinters coexist and interact during the smelting process in the blast furnace. The reduction kinetics of a single sample cannot directly guide the blast furnace smelting production of CVTO. Therefore, this study aims to reveal the metallurgical reaction kinetics of CVTO smelting. The feasibility and qualification conditions of large pellet ratio and CO$_2$ injection were explored.

2. Materials and Methods

2.1. Materials Preparation

At present, high–basicity sinter/pellet, acid pellet, and lump ore are still the main burden structures for CVTO smelting in blast furnaces. Chromia–bearing vanadiferous titanomagnetite ore ores were used to prepare the experimental samples, and they were mixed with the acid pellets, basic pellets, and basic sinters with a mass ratio of 2.56:1:2 to keep the slag basicity required from actual production (CaO/SiO$_2$ is about 1.1). The acidic CVT pellets were prepared in air by prebaking at 900 °C for 15 min and then calcining at 1200 °C for 20 min. The basic pellets were produced by prebaking at 950 °C for 15 min and then calcining at 1250 °C for 20 min. The X–ray diffraction (XRD) pattern and chemical components of concentrate powder, acid pellet (AP), basic sinter (BS), and basic pellet (BP) are shown in Figure 1.

![Figure 1. XRD pattern of Cr–bearing vanadiferous titanomagnetite ore.](image)
2.2. Apparatus and Methods

According to the national test standard GB/T 34211–2017, the experiments of softening-melting-dripping performance and thermogravimetric (TG) reduction were mainly carried out in a laboratory-grade blast furnace, as shown in Figure 2. In total, 500 g samples were sandwiched between two sets of 100 g coke and placed in a graphite crucible (inner diameter 75 mm × height 180 mm). Their reaction conditions are shown in Table 1. The CO\textsubscript{2} concentration in HCG was set to 0 vol.%, 10 vol.%, 20 vol.%, and 30 vol.%. The temperature in the TG experiment was used as the side temperature of the furnace for testing. Therefore, the central temperature and side temperature of the furnace were tested, as shown in Figure 3. The average temperature difference between the side temperature and the central temperature was 100 °C.

Table 1. Reaction conditions.

| Central Temperature   | RT–500 °C | 500–1300 °C | 1300 °C–RT |
|-----------------------|-----------|-------------|------------|
| Heating rate          | 10 °C/min | 5 °C/min    | 5 °C/min   |
| Operating time        | 50 min    | 160 min     | >300 min   |
| Reaction gas          | N\textsubscript{2} 100% | CO/CO\textsubscript{2}/N\textsubscript{2} (Total 5 L/min) | Ar 100% |

RT: room temperature.

Figure 2. Apparatus: (a) softening–melting–dripping performances test furnace; (b) thermogravimetric reduction furnace.
will move downward. Correspondingly, \[T_{40}–T_4\] and \[Td–Ts\] are reduced by 9 °C and 22 °C, respectively, which means that the positions of the softening zone and the melting–dripping zone \([Td–Ts]\) show the position of the lump zone and the cohesive zone.

2.3. Characterizations

The phases of slag and iron were analyzed by X–ray diffraction (X’ Pert Pro; PANalytical, Almelo, The Netherlands) using Cu Ka radiation (wavelength = 1.5406 Å) at a setting of 40 kV and 40 mA. The chemical compositions of ground samples were analyzed by inductively coupled plasma–atomic emission spectroscopy (ICP–AES, Optima 8300DV; PerkinElmer, Waltham, MA, USA) and X–ray fluorescence spectrometer (XRF, ZSXPrimus II; Rigaku, Tokyo, Japan). The chemical properties of surface elements were analyzed by X–ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo, Waltham, MA, USA). The scanning electron microscope (SEM, Ultra Plus; Carl Zeiss GmbH, Jena, Germany) was used to detect the microstructure of the unground slag with a backscattering detector (BSE). The diagram of the Ti–C–O–N predominant region of the obtained slag was calculated by Factsage (8.0, Centre for Research in Computational Thermochemistry, Montreal, QC, Canada).

3. Results and Discussion

3.1. Effect of High–Temperature CO$_2$–Containing Gas in the Thermodynamic Smelting Process

The effect of the injected CO$_2$ concentration on the softening–melting–dripping characteristics of CVTO was explored, and the results are shown in Figure 4. It can be found that as the concentration of the injected CO$_2$ increases from 0 vol.% to 30 vol.%, \(T_d\), \(T_{40}\), \(T_s\), and \(T_d\) show a trend of first rising and then falling. When the concentration of the injected CO$_2$ is 10 vol.%, \(T_d\), \(T_{40}\), \(T_s\), and \(T_d\) increase by 47 °C, 38 °C, 33 °C, and 11 °C, respectively, which means that the positions of the softening zone and the dripping zone of the charge will move downward. Correspondingly, \([T_{40}–T_d]\) and \([Td–Ts]\) are reduced by 9 °C and 22 °C, respectively, which means that the widths of the softening zone and
the dripping zone have become smaller, which is beneficial to improve gas permeability instead of charge reduction. When the injected CO₂ concentration is 30 vol.%, the dripping temperature $T_d$ is 1361 °C, which means that the premature separation of molten slag and iron is not conducive to the separation and migration of valuable elements. Therefore, when the injected CO₂ concentration is 20 vol.%, the softening–melting–dripping characteristics can be close to the case in which the injected CO₂ concentration is 0 vol.%, which is beneficial to realize the reuse of CO₂, save energy and reduce emissions [3–5,13,21–24].

Figure 4. Softening–melting–dripping performances with different CO₂ ratios.

3.2. Isothermal and Nonisothermal Kinetics of High-Temperature CO₂–Containing Gas in the Polymetallic Reduction Process

Multi-interface isothermal and nonisothermal kinetics experiments can further determine the influence of CO₂ concentration on the reduction rate in the CVTO smelting process. The nonisothermal kinetic process can reflect the complexity and activity of the interfacial reaction at different stages in the experiments of the softening–melting–dripping characteristics. As shown in Figure 5, the results of nonisothermal kinetics show that the weight change is synchronized with the softening–melting–dripping experiments. It can be found that as the temperature increases, the nonisothermal kinetics curve shows a nonlinear change, which means that complex multi-interface reactions may occur simultaneously during the CVTO reduction smelting process, such as the gas–solid reaction in the lump zone, the solid–solid/gas reaction in the softening zone, and the liquid–liquid/solid/gas reaction in the dripping zone.
Figure 5. Multi–interface nonisothermal kinetics mass change curves.

Figure 6 shows the weight change of the sample’s multi–interface isothermal kinetics. When the side temperature increases from 900 °C to 1300 °C, it is estimated that the corresponding core temperature rises from 800 °C to 1200 °C. The experimental results of isothermal kinetics correspond to the reaction stages of the lump zone and the softening zone in the softening–melting–dripping characteristic experiments. The isothermal kinetics curve shows a linear trend, which indicates that the gas–solid reaction and the solid–solid interface reaction that mainly occur in the lump zone and the softening zone may not be restricted by the diffusion law. Therefore, it can be considered that the weight loss of the charge is caused by complex multi–interface reactions, and the valuable metal oxides may also participate in the reoxidation reaction in the reduction process.

Figure 6. Multi–interface isothermal kinetics mass change curves.
In order to further analyze the nonisothermal and isothermal kinetics curves, the weight loss rate $\alpha$ can be set to indicate the reduction rate of the charge, and its definition is shown in Equation (1).

$$\alpha = \frac{\Delta m}{m_0},$$

(1)

where $\Delta m$ is the weight loss of the sample, and $m_0$ is the original weight of the sample.

According to the Avrami–Erofeev model (Equation (2)), it can be judged that the reduction process of the sample conforms to the $n$–order reaction.

$$\ln[-\ln(1-\alpha)] = n \ln t + n \ln k,$$

(2)

where $k$ is the reaction rate constant, $t$ is the time (min), and $n$ is the Avrami exponent. Figures 7 and 8 show the mapping and fitting of $\ln[-\ln(1-\alpha)] - \ln t$ to nonisothermal and isothermal kinetics, respectively. Tables 2 and 3 are the ln–ln fitting parameters of non–isothermal and isothermal kinetics, respectively. The slope of the fitted line represents the Avrami exponent $n$. The fitting slope of ln–ln for nonisothermal kinetics is between 1.3 and 2.6, while the fitting slope of ln–ln for isothermal kinetics is between 0.67 and 1.02. Therefore, according to the commonly used kinetics models and the $n$ value in Table 4, the CG2, A2, and A3 models can be used to describe the nonisothermal reduction kinetics process of CVTO, which means that the reduction kinetics model is more suitable for the phase interface reaction model than the random 3D/2D unreacted core model as the concentration of the injected CO$_2$ increases. In addition, the isothermal reduction kinetics process of CVTO is more in line with the D$1$, R$1$, and CG3 models, which means that it may also be suitable for a diffusion model at temperatures where chemical reactions are not active [13,15–20,25].

Figure 7. ln–ln fitting curves of multi–interface nonisothermal kinetics.
The activation energy of nonisothermal kinetics is generally solved by the Coats–Redfern equation. When \( n \neq 1 \), the C–R equation is as follows:

\[
\ln\left(\frac{1 - (1 - \alpha)^{1/n}}{(1 - \alpha)^{1/n}}\right) = kT
\]
\[ \ln \left[ \frac{1 - (1 - n)^{1-n}}{(1-n)^2} \right] = \ln \left[ \frac{(AR/\beta E_a)(1 - (2RT/E_a))}{1 - E_a/RT} \right], \]

where \( \beta \) is the heating rate (K/min), \( R \) is the ideal gas constant 8.314 J mol\(^{-1}\) K\(^{-1}\), and \( T \) is the reduction temperature (K). In \( \left[ 1 - (1 - n)^{1-n}/(1-n)^2 \right] \) vs. \( 1/T \) is plotted in Figure 9. As shown in Table 5, as the concentration of the injected CO\(_2\) increases, the apparent activation energy reaches the minimum value of 75.58 kJ mol\(^{-1}\) when CO\(_2\) is 20 vol.\%, which means that injecting an appropriate concentration of CO\(_2\) can also effectively promote the smelting process of CVTO.

![Figure 9. Coats–Redfern fitting curves of multi–interface nonisothermal kinetics.](image)

**Table 5.** Line fitting data of nonisothermal \( E_a \).

| Conditions | 1  | 2  | 3  | 4  |
|------------|----|----|----|----|
| Slope      | -10.217 | -14.273 | -9090 | -14,952 |
| Intercept  | 7.80 | 7.80 | 7.80 | 7.80 |
| \( R^2 \)  | 0.84 | 0.95 | 0.92 | 0.96 |
| \( E_a \)  | 84.94 | 118.67 | 75.58 | 124.31 |

For the activation energy calculation of isothermal kinetics, according to Tables 3 and 4, it can be seen that the isothermal reduction process satisfies the CG\(_3\) model. Therefore, the weight loss rate \( \alpha \) of the isothermal reduction process is fitted according to \( 1 - (1 - a)^{1/3} - t \), and the result is shown in Figure 10. The slope of the fitted straight line is the \( k \) value, and the fitting parameters of the isothermal reduction kinetics are shown in Table 6.

![Figure 10. Coats–Redfern fitting curves of multi–interface isothermal kinetics.](image)

**Table 6.** Line fitting data of isothermal \( E_a \).

| Conditions | 1  | 2  | 3  | 4  |
|------------|----|----|----|----|
| Slope      | -10.81 | -14.952 | -9090 | -14,952 |
| Intercept  | 9.46 | 10.81 | 10.81 | 10.81 |
| \( R^2 \)  | 0.84 | 0.92 | 0.92 | 0.92 |
| \( E_a \)  | 84.94 | 118.67 | 75.58 | 124.31 |

According to the Arrhenius equation (Equation (4)), \( \ln k \) and \( 1/T \) can be further fitted, and the fitted straight line is shown in Figure 11. The slope of the fitted straight line can be solved according to Equation (4), and the apparent activation energy of the isothermal kinetics process is 121.93 kJ mol\(^{-1}\). When the apparent activation energy is greater than 400 kJ mol\(^{-1}\), the restrictive step is determined by the interface chemical reaction. When the apparent activation energy is less than 150 kJ mol\(^{-1}\), the restrictive step is controlled by diffusion. Therefore, the restrictive step of this isothermal kinetics process is mainly determined by diffusion.

\[ \ln k = \ln A - E_a/RT, \] (4)
3.3. Reaction Mechanism of High–Temperature CO2–Containing Gas in the Polymetallic Smelting

According to the XRD analysis of the raw materials in Figure 1, CVTO pellets are mainly composed of Fe$_2$O$_3$, Fe$_3$O$_4$, and Fe$_2$TiO$_5$, while CVTO sinters are mainly composed of perovskite (CaO·TiO$_2$), haplotypite ($m$Fe$_2$O$_3$$n$FeO·TiO$_2$), and titanomagnetite ($m$Fe$_3$O$_4$$n$(2FeO·TiO$_2$)). The reduction reactions of these multimetallic oxides antagonize each other, which makes the results of softening–melting–dripping characteristic experiments and kinetics experiments more complicated. The CVTO smelting process with CO$_2$ injection is shown in Figure 12. The whole reduction process can be divided into...
three stages. First, in the lump zone where the direct reduction reactions mainly occur, the complex Fe–Ti–O compound in CVTO is first reduced to Fe–O and Ti–O compounds, and the charge begins to soften. Secondly, the cohesive zone includes the softening and melting zone, in which the indirect reduction reactions are mainly carried out. Iron oxide and titanium oxide are gradually reduced to low–valence oxides.

In particular, titanium oxide is excessively reduced to titanium carbide, titanium nitride and titanium carbonitride, and FeO participates in the formation of a low–melting–point multielement slag system. Due to the presence of titanium carbonitride, the molten slag begins to form and gradually thickens, and then molten iron appears. Finally, the dripping zone, also known as the high–temperature zone, or oxidation zone, contains the bottom of the melting zone and the raceway at the tuyere. After the carburizing reaction, the molten iron begins to drip, and the slag phase tends to separate from the molten iron and stabilize to form the final slag and drop. During the dripping process, the reduced metals and low–valence metal compounds react with O2 and CO2 in the raceway, and part of the valuable metal compounds will be reoxidized [1,2,22,23].

\[
\begin{align*}
3\text{TiO}_2 + C &= \text{Ti}_3\text{O}_5 + \text{CO}, \; \Delta G_1^\Theta = 193,673 - 183.84T, \quad (5) \\
2\text{Ti}_3\text{O}_5 + C &= 3\text{Ti}_2\text{O}_3 + \text{CO}, \; \Delta G_2^\Theta = 258,509 - 170.03T, \quad (6) \\
\text{Ti}_2\text{O}_3 + 3C &= \text{TiC} + 2\text{CO}, \; \Delta G_3^\Theta = 290,718 - 173.59T, \quad (7) \\
\text{Ti}_3\text{O}_5 + 8C &= 3\text{TiC} + 5\text{CO}, \; \Delta G_4^\Theta = 1,281,880 - 796.31T, \quad (8) \\
\text{Ti}_2\text{O}_3 + 5C &= 2\text{TiC} + 3\text{CO}, \; \Delta G_5^\Theta = 793,515 - 498.65T, \quad (9) \\
2\text{TiO}_2 + 4C + N_2 &= 2\text{TiN} + 4\text{CO}, \; \Delta G_6^\Theta = 758,378 - 515.08T, \quad (10) \\
3\text{TiO}_2 + 7C + N_2 &= 2\text{TiN} + \text{TiC} + 6\text{CO}, \; \Delta G_7^\Theta = 1,263,266 - 852.7T, \quad (11) \\
\text{TiO}_2 + \text{CaO} &= \text{CaO} \cdot \text{TiO}_2, \; \Delta G_8^\Theta = -79,900 - 3.35T, \quad (12) \\
3\text{CaTiO}_3 + N_2 + 7C &= 2\text{TiN} + \text{TiC} + 3\text{CaO} + 6\text{CO}, \; \Delta G_9^\Theta = 1,487,223 - 807.44T, \quad (13)
\end{align*}
\]

Figure 12. CVTO smelting and reduction processes in blast furnace.
A thermodynamic diagram of the reaction involving titanium oxide drawn according to the chemical equations from Equations (5)–(13) is shown in Figure 13. It can be seen that titania is one of the complex compounds with a multimetallic structure in CVTO, and its reduction process greatly affects the softening-melting-dripping performance and kinetic process of CVTO smelting. In the lump zone with a temperature ranging from 700 °C to 1200 °C, titania mainly participates in the reaction with CaO to form perovskite and the reaction with C to form low-valence titanium oxide. At this time, due to a lower temperature and slower solid–solid interface reactions, gas–solid reactions and gas–phase diffusion dominates the reaction process. When the temperature rises to about 1242 °C, titania is almost completely melted, and the tendency to react with coke to form low-valence titanium oxide exceeds the tendency to combine with CaO to form perovskite. When the temperature increases to 1326 °C, a large amount of titanium carbide, titanium nitride, and titanium carbonitride are formed due to the combined action of C and N2 of the low-valence titanium oxide. It can be found that during the entire reaction process, the perovskite formed by the combination of TiO2 and CaO is very stable, and it is difficult to reduce and decompose into other titanium compounds even at higher temperatures. The properties of the titanium carbonitride generated in the high-temperature zone (dripping zone) on molten slag and molten iron will cause a sharp increase in viscosity, foaming, and difficulty in separating slag and iron, which will be manifested by a worsening smelting index and higher apparent activation energy. Figure 14 shows the diagram of the predominance area of Ti–C–N–O calculated by Factsage 8.0. It can be found that the higher the partial pressure of CO2 in the reducing atmosphere is, the more titania in the slag system tends to form higher valence titanium oxide, and the content of TiC will decrease. When there is only a small amount of coke and nitrogen in the burden, TiC and TiN will inevitably be produced. In addition, for the C–CO–CO2 system, increasing the partial pressure of CO2 can more effectively inhibit the excessive reduction of TiO2 than increasing CO.

![Figure 13. Gibbs free energy of Ti–compound reduction reactions vs. temperature.](image-url)
Figure 14. Predominant region diagrams of Ti–C–N–O system.

Figure 15 shows the change in the valence state of the titanium compound during the isothermal reduction process. It can be found that as the temperature increases, the multivalent titanium compound tends to decrease. When the temperature increases from 900 °C to 1100 °C, the Ti$^{2+}$ composition of the titanium compounds within the range of B.E. from 456 eV to 461.5 eV is gradually simplified, while the Ti$^{3+}$ composition of the titanium compound within the range of B.E. from 461.5 eV to 467 eV is gradually complicated, which means that the titanium oxide initially combined with iron oxide is gradually decomposed under the action of gas–solid reduction. At the same time, the reduced titanium dioxide is gradually reduced to various low–valence titanium oxides. When the temperature increases from 1200 °C to 1300 °C, there is a large amount of FeO$^x$ in the slag. Under the action of high oxidation potential, the further reduction of titanium oxide is inhibited and tends to stabilize in a higher valence state.
Therefore, combined with production practice, it can be considered that it is feasible to inject high-temperature CO$_2$-containing gas into the CVTO blast furnace to replace hot air. The additional CO$_2$ injection will not inhibit the progress of smelting. However, the diffusion kinetics of CO$_2$ at the slag-coke interface in the cohesive zone still needs to be further explored to prove the change of the interface oxygen potential.

4. Conclusions

According to the thermodynamic smelting experiments and the nonisothermal and isothermal kinetics experiments of the chromia-bearing vanadiferous titanomagnetite ore, it is believed that the preferable CO$_2$ concentration in the injected high-temperature gas is 20 vol.%. The experimental results of softening-melting-dripping characteristics show that as the concentration of the injected CO$_2$ increases from 0 vol.% to 30 vol.%, the softening zone [$T_{40}-T_{4}$] is decreased from 109 °C to 97 °C, and the melting-dripping zone [$T_{d}-T_{s}$] is decreased from 196 °C to 162 °C. The nonisothermal reduction kinetics process of CVTO can be described by CG$_2$, A$_2$, and A$_3$ models. When CO$_2$ concentration is 20 vol.%, the minimum apparent activation energy of nonisothermal kinetics reaches 75.58 kJ·mol$^{-1}$.

According to the fitting isothermal parameters of $1 - (1 - \alpha)^{1/3} - t$ (CG$_3$ model), its apparent activation energy is 121.93 kJ·mol$^{-1}$ (less than 150 kJ·mol$^{-1}$), which means that
the restrictive step of the polymetallic reaction is mainly determined by diffusion, and the apparent activation energy of the isothermal kinetics process is 121.93 kJ·mol⁻¹.

Based on thermodynamics and characterizations, the reaction mechanism of high-temperature CO₂–containing gas injection in the polymetallic smelting process was investigated. It can be found that the higher the partial pressure of CO₂ in the reducing atmosphere, the more titania in the slag system tends to form higher valence titanium oxide, and the content of TiC will decrease. When there is only a small amount of coke and nitrogen in the burden, TiC and TiN will inevitably be produced. In addition, it can be found that for the C–CO–CO₂ system, increasing the partial pressure of CO₂ can more effectively inhibit the excessive reduction of TiO₂ than increasing CO. All of these provide a theoretical argument for the possibility of injecting high-temperature CO₂–containing gas into the chromia–bearing vanadiferous titanomagnetite ore blast furnace.

Author Contributions: Data curation, software, formal analysis, visualization, writing—original draft preparation, writing—review and editing, H.S.; data curation, writing—review and editing, supervision, G.C., J.L. and J.Z.; conceptualization, funding acquisition, investigation, project administration, resources, supervision, X.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grant No. 51674084, No. ZX20200031, and No. 2017YFB0304304).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing not applicable.

Acknowledgments: Special thanks are due to the instrumental or data analysis from the Analytical and Testing Center, Northeastern University. The authors would like to thank EditSprings (https://www.editsprings.com/ (accessed on 12 June 2021)) for providing professional language services.

Conflicts of Interest: The authors declare that there is no conflict of interest.

References
1. Du, H.G. Principle of Smelting Vanadium-Titanium Magnetite, 1st ed.; Science Press: Beijing, China, 1996.
2. Xue, X.Y.; Yang, S.T.; Zhang, Y. Blast Furnace Process Smelting Chromium-Containing Vanadia-Titania Magnetite: Theory and Practice, 1st ed.; Science Press: Beijing, China, 2020.
3. Cheng, G.J.; Xue, X.X.; Jiang, T.; Duan, P.N. Effect of TiO₂ on the Crushing Strength and Smelting Mechanism of High-Chromium Vanadium-Titanium Magnetite Pellets. Metall. Mater. Trans. B 2016, 47, 1713–1726. [CrossRef]
4. Li, T.L.; Sun, C.Y.; Lan, D.; Song, J.; Song, S.; Wang, Q. Effect of Mineral Elements Migration on Softening-melting Properties of Ti-bearing High Basicity Sinter. ISIJ Int. 2019, 59, 243–252. [CrossRef]
5. Liu, J.X.; Cheng, G.J.; Liu, Z.G.; Chu, M.S.; Xue, X.X. Softening and melting properties of different burden structures containing high chromic vanadium titano-magnetite. Int. J. Miner. Process. 2015, 142, 113–118. [CrossRef]
6. Yue, H.R.; He, Z.W.; Jiang, T.; Duan, P.N.; Xue, X.X. Rheological Evolution of Ti-Bearing Slag with Different Volume Fractions of TiN. Metall. Mater. Trans. B 2018, 49, 2118–2127. [CrossRef]
7. Chen, W.; Yin, X.; Ma, D. A bottom-up analysis of China’s iron and steel industrial energy consumption and CO₂ emissions. Appl. Energy 2014, 136, 1174–1183. [CrossRef]
8. Chung, W.; Roh, K.; Lee, J.H. Design and evaluation of CO₂ capture plants for the steelmaking industry by means of amine scrubbing and membrane separation. Int. J. Greenh. Gas Control 2018, 74, 259–270. [CrossRef]
9. Wang, H.; Zhu, R.; Wang, X.; Li, Z. Utilization of CO₂ in metallurgical processes in China. Miner. Process. Extr. Metall. 2017, 126, 47–53. [CrossRef]
10. Zhang, Q.; Li, Y.; Xu, J.; Jia, G.Y. Carbon element flow analysis and CO₂ emission reduction in iron and steel works. J. Clean. Prod. 2018, 172, 709–723. [CrossRef]
11. Zhu, R. Theory and Practice of Carbon Dioxide Steelmaking, 1st ed.; Science Press: Beijing, China, 2019.
12. Song, H.L.; Zhang, J.P.; Cheng, G.J.; Yang, S.T.; Xue, X.X. Study on the High-temperature Properties of High-titania Slags produced with Cr-bearing Vanadia-titania Magnetite Smelting in Blast Furnace. Surf. Interfaces 2020, 21, 100767. [CrossRef]
13. Halli, P.; Taskinen, P.; Eric, R.H. Mechanisms and Kinetics of Solid State Reduction of Titano Magnetite Ore with Methane. J. Sustain. Metall. 2017, 3, 191–206. [CrossRef]
14. Liu, S.S.; Guo, Y.F.; Qiu, G.Z.; Jiang, T.; Chen, F. Solid-state reduction kinetics and mechanism of pre-oxidized vanadium-titanium magnetite concentrate. Trans. Nonferrous Met. Soc. China 2014, 24, 3372–3377. [CrossRef]
15. Lu, C.Y.; Zou, X.L.; Lu, X.G.; Xie, X.L.; Zheng, K.; Xiao, W.; Cheng, H.W.; Li, G.S. Reductive kinetics of Panzhihua ilmenite with hydrogen. *Trans. Nonferrous Met. Soc. China* 2016, 26, 3266–3273. [CrossRef]

16. Lv, W.; Lv, X.W.; Zhang, Y.Y.; Li, S.P.; Tang, K.; Song, B. Isothermal oxidation kinetics of ilmenite concentrate powder from Panzhihua in air. *Powder Technol.* 2017, 320, 239–248. [CrossRef]

17. Pan, F.; Zhu, Q.S.; Du, Z.; Sun, H.Y. Oxidation Kinetics, Structural Changes and Element Migration during Oxidation Process of Vanadium-titanium Magnetite Ore. *J. Iron Steel Res. Int.* 2016, 23, 1160–1167. [CrossRef]

18. Sarkar, B.K.; Samanta, S.; Dey, R.; Das, G.C. A study on reduction kinetics of titaniferous magnetite ore using lean grade coal. *Int. J. Miner. Process.* 2016, 152, 36–45. [CrossRef]

19. Sui, Y.L.; Guo, Y.F.; Jiang, T.; Qiu, G.Z. Reduction kinetics of oxidized vanadium titanomagnetite pellets using carbon monoxide and hydrogen. *J. Alloys Compd.* 2017, 706, 546–553. [CrossRef]

20. Zhang, J.L.; Xing, X.D.; Cao, M.M.; Jiao, K.X.; Wang, C.L.; Ren, S. Reduction Kinetics of Vanadium Titano-Magnetite Carbon Composite Pellets Adding Catalysts Under High Temperature. *J. Iron Steel Res. Int.* 2013, 20, 1–7. [CrossRef]

21. Nandy, B.; Chandra, S.; Bhattacharjee, D.; Ghosh, D. Assessment of blast furnace behaviour through softening-melting test. *Ironmak. Steelmak.* 2006, 33, 111–119. [CrossRef]

22. Liu, X.L.; Honeyands, T.; Evans, G.; Zulli, P.; O’Dea, D. A review of high-temperature experimental techniques used to investigate the cohesive zone of the ironmaking blast furnace. *Ironmak. Steelmak.* 2019, 46, 953–967. [CrossRef]

23. Xiang, J.Y.; Wang, J.; Li, Q.J.; Shan, C.; Qiu, G.B.; Yu, W.Z.; Lv, X.W. Slag-foaming phenomenon originating from reaction of titanium-bearing blast furnace slag: Effects of TiO₂ content and basicity. *Can. Metall. Q.* 2020, 59, 151–158. [CrossRef]

24. Li, W.; Wang, N.; Fu, G.Q.; Chu, M.S.; Zhu, M.Y. Influence of TiO₂ addition on the oxidation induration and reduction behavior of Hongge vanadium titanomagnetite pellets with simulated shaft furnace gases. *Powder Technol.* 2018, 326, 137–145. [CrossRef]

25. Zhao, L.S.; Wang, L.N.; Chen, D.S.; Zhao, H.X.; Liu, Y.H.; Qi, T. Behaviors of vanadium and chromium in coal-based direct reduction of high-chromium vanadium-bearing titanomagnetite concentrates followed by magnetic separation. *Trans. Nonferrous Met. Soc. China* 2015, 25, 1325–1333. [CrossRef]