Article

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

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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 [T_{40} – T_4] decreased from 109 °C to 97 °C, and the range of droplet temperature [T_d – T_s] 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 nonisothermal reduction rate, the optimal CO₂ concentration in the fuel gas was considered to be 20 vol.%. The isothermal parameters were fitted according to $1 - (1 - \alpha)^{1/3} - t$ (CG₃ 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 polymetallic 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.

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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.

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 CO₂ 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 ₂ 100%	CO/CO ₂ /N ₂ (Total 5 L/min)	Ar 100%

RT: room temperature.

Figure 2. Apparatus: (a) softening–melting–dripping performances test furnace; (b) thermogravimetric reduction furnace.

Figure 3. Central temperature and side temperature of the test furnace.

T_4 denotes the softening start temperature with a burden shrinkage rate of 4%. T_{40} represents the softening end temperature with a burden shrinkage rate of 40%. T_s is the melting start temperature as the furnace pressure sharply raised to 500 Pa. T_d is the dripping start temperature as the weight of the dropped substance reached 20 g. The softening zone [$T_{40}-T_4$] and the melting–dripping zone [T_d-T_s] 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 K α 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 CO₂-Containing Gas in the Thermodynamic Smelting Process

The effect of the injected CO₂ 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 CO₂ increases from 0 vol.% to 30 vol.%, T_4 , T_{40} , T_s , and T_d show a trend of first rising and then falling. When the concentration of the injected CO₂ is 10 vol.%, T_4 , 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, [$T_{40}-T_4$] and [T_d-T_s] 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 CO_2 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 CO_2 concentration is 20 vol.%, the softening–melting–dripping characteristics can be close to the case in which the injected CO_2 concentration is 0 vol.%, which is beneficial to realize the reuse of CO_2 , save energy and reduce emissions [3–5,13,21–24].

Figure 4. Softening–melting–dripping performances with different CO_2 ratios.

3.2. Isothermal and Nonisothermal Kinetics of High–Temperature CO_2 –Containing Gas in the Polymetallic Reduction Process

Multi–interface isothermal and nonisothermal kinetics experiments can further determine the influence of CO_2 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 α can be set to indicate the reduction rate of the charge, and its definition is shown in Equation (1).

$$\alpha = \Delta m / m_0, \quad (1)$$

where Δm 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.

$$\ln [-\ln (1-\alpha)] = n \ln t + n \ln k, \quad (2)$$

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 CG_2 , A_2 , and A_3 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 CG_3 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.

Figure 8. ln–ln fitting curves of multi-interface isothermal kinetics.

Table 2. Line fitting values of nonisothermal data.

Conditions	1	2	3	4
Slope	2.5804	2.2243	1.5415	2.287
Intercept	−13.871	−13.326	−9.635	−14.34
R ²	0.893	0.96	0.9637	0.9393

Table 3. Line fitting values of isothermal data.

Conditions	1	2	3	4	5
Slope	0.9985	0.6783	0.808	0.8905	1.0151
Intercept	−8.5879	−6.7163	−6.2483	−5.6679	−5.8198
R ²	0.9579	0.9891	0.9866	0.9991	0.9998

Table 4. Common kinetics models.

Type	$G(\alpha)$	n
D ₁	$\alpha^2 = kt$	0.62
D ₂	$(1 - \alpha) \ln(1 - \alpha) + \alpha = kt$	0.57
D ₃	$[1 - (1 - \alpha)^{1/3}]^2 = kt$	0.54
D ₄	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3} = kt$	0.57
CG ₂	$1 - (1 - \alpha)^{1/2} = kt$	1.11
CG ₃	$1 - (1 - \alpha)^{1/3} = kt$	1.07
R ₁	$-\ln(1 - \alpha) = kt$	1.00
A ₂	$[-\ln(1 - \alpha)]^{1/2} = kt$	2.00
A ₃	$[-\ln(1 - \alpha)]^{1/3} = kt$	3.00

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:

$$\ln \{[1 - (1 - \alpha)^{1-n}] / [(1 - n) T^2]\} = \ln \{(AR/\beta E_a) [1 - (2RT/E_a)]\} - E_a/RT, \quad (3)$$

where β is the heating rate (K/min), R is the ideal gas constant $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and T is the reduction temperature (K). $\ln \{[1 - (1 - \alpha)^{1-n}] / [(1 - n) T^2]\}$ 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 $75.58 \text{ kJ}\cdot\text{mol}^{-1}$ 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.

Table 5. Line fitting data of nonisothermal E_a .

Conditions	1	2	3	4
Slope	−10,217	−14,273	−9090	−14,952
Intercept	−9.46	−7.80	−10.81	−8.05
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 α of the isothermal reduction process is fitted according to $1 - (1 - \alpha)^{1/3} = t$, 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.

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 $121.93 \text{ kJ}\cdot\text{mol}^{-1}$. When the apparent activation energy is greater than $400 \text{ kJ}\cdot\text{mol}^{-1}$, the restrictive step is determined by the interface chemical reaction. When the apparent activation energy is less than $150 \text{ kJ}\cdot\text{mol}^{-1}$, the restrictive step is controlled by diffusion. Therefore, the restrictive step of this isothermal kinetics process is mainly determined by diffusion.

$$\ln k = \ln A - E_a/RT, \quad (4)$$

Figure 10. CG₃ model fitting curves of multi-interface isothermal kinetics.

Table 6. Line fitting data of isothermal E_a .

Conditions	1	2	3	4	5
Slope ($\times 10^{-5}$)	5	8	20	60	100
Intercept ($\times 10^{-4}$)	7	16	24	39	0.02
R^2	0.9549	0.9902	0.9904	0.999	0.9999

Figure 11. E_a fitting curves of multi-interface isothermal kinetics.

3.3. Reaction Mechanism of High-Temperature CO_2 -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_2O_3 , Fe_3O_4 , and Fe_2TiO_5 , while CVTO sinters are mainly composed of perovskite ($\text{CaO} \cdot \text{TiO}_2$), haptypite ($m\text{Fe}_2\text{O}_3 \cdot n\text{FeO} \cdot \text{TiO}_2$), and titanomagnetite ($m\text{Fe}_3\text{O}_4 \cdot n(2\text{FeO} \cdot \text{TiO}_2)$). 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.

Figure 12. CVTO smelting and reduction processes in blast furnace.

In particular, titanium oxide is excessively reduced to titanium carbide, titanium nitride and titanium carbonitride, and FeO_x 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 O_2 and CO_2 in the raceway, and part of the valuable metal compounds will be reoxidized [1,2,22,23].

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. Then, as 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.

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 $\text{Ti}2p_{3/2}$ composition of the titanium compounds within the range of B.E. from 456 eV to 461.5 eV is gradually simplified, while the $\text{Ti}2p_{1/2}$ 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.

Figure 15. XPS pattern of samples after CVTO isothermal reduction.

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 $\text{kJ}\cdot\text{mol}^{-1}$. According to the fitting isothermal parameters of $1 - (1 - \alpha)^{1/3} - t$ (CG_3 model), its apparent activation energy is 121.93 $\text{kJ}\cdot\text{mol}^{-1}$ (less than 150 $\text{kJ}\cdot\text{mol}^{-1}$), 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 $121.93 \text{ kJ}\cdot\text{mol}^{-1}$.

Based on thermodynamics and characterizations, the reaction mechanism of high-temperature CO_2 -containing gas injection in the polymetallic smelting process was investigated. It can be found that the higher the partial pressure of CO_2 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– CO_2 system, increasing the partial pressure of CO_2 can more effectively inhibit the excessive reduction of TiO_2 than increasing CO. All of these provide a theoretical argument for the possibility of injecting high-temperature CO_2 -containing gas into the chromia-bearing vanadiferous titanomagnetite ore blast furnace.

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