



Article

Effects of Basicity and MgO in Slag on the Behaviors of Smelting Vanadium Titanomagnetite in the Direct Reduction-Electric Furnace Process

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Abstract: The effects of basicity and MgO content on reduction behavior and separation of iron and slag during smelting vanadium titanomagnetite by electric furnace were investigated. The reduction behaviors affect the separation of iron and slag in the direct reduction-electric furnace process. The recovery rates of Fe, V, and Ti grades in iron were analyzed to determine the effects of basicity and MgO content on the reduction of iron oxides, vanadium oxides, and titanium oxides. The chemical compositions of vanadium-bearing iron and main phases of titanium slag were detected by XRF and XRD, respectively. The results show that the higher level of basicity is beneficial to the reduction of iron oxides and vanadium oxides, and titanium content dropped in molten iron with the increasing basicity. As the content of MgO increased, the recovery rate of Fe increased slightly but the recovery rate of V increased considerably. The grades of Ti in molten iron were at a low level without significant change when MgO content was below 11%, but increased as MgO content increased to 12.75%. The optimum conditions for smelting vanadium titanomagnetite were about 11.38% content of MgO and quaternary basicity was about 1.10. The product, vanadium-bearing iron, can be applied in the converter steelmaking process, and titanium slag containing 50.34% TiO₂ can be used by the acid leaching method.

Keywords: basicity; MgO; vanadium titanomagnetite; direct reduction-electric furnace; iron-slag separation

1. Introduction

Vanadium titanomagnetite ore is a valuable resource which contains rich titanium, vanadium, and other metal elements. The Panxi region of China is rich in vanadium titanomagnetite resources with reserves of about 9.66 billion tons [1]. The proven deposits of titanium and vanadium account for 35.17% and 11.6% of world total reserves, respectively [2]. The blast furnace process has been used to utilize vanadium titanomagnetite resources since the 1970s in China [3], but the byproduct of the blast furnace, titanium slag which contains 22%–25% TiO₂, is difficult to be recovered on a large scale. Obviously, the titanium resource is wasted, to be stockpiled without effective utilization, and simultaneously causes environmental pollution. Actually, the recovery rates of Fe, V, and Ti of vanadium titanomagnetite under the main blast furnace process are about 70%, 47%, and 10%–20%, respectively [4]. Therefore, the key to raise up the utilization level of vanadium titanomagnetite is to increase the recovery rate of Ti. There are many methods [2,5–8] developed, or under development, including direct reduction-electric furnace smelting, sodium salt roasting-direct reduction-electric furnace smelting, and direct reduction-magnetic separation, and so on.

Compared with the other methods, which are still under investigation due to technological problems, the direct reduction-electric furnace smelting process has many advantages and has been

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commercialized in South Africa and New Zealand successfully [9]. However, reductions of vanadium oxides and titanium oxides in vanadium titanomagnetite and the separation of titanium slag from iron are difficult to control in this process. The separation of iron and slag would be difficult if titanium oxides were over-reduced. High basicity slag was used to solve this problem in electric furnace smelting in South Africa and New Zealand. As a result, the titanium slag contained about 30%–33% TiO_2 is obtained, but without effective recovery methods.

Previous research indicated that titanium resources could be recovered by acid leaching methods when the titanium slag contained about 50% TiO₂ [1]. Thus, the optimum composition of titanium slag which contained about 50% TiO₂ should be found. Furthermore, low melting temperature and low viscosity of titanium slag are needed to make the separation of titanium slag from iron successful. Fluxes and additives are commonly added to ensure the electric furnace smelting completes successfully [10]. CaO and MgO are important additives for the electric furnace process as well as blast furnace process [11,12]. Generally, basicity and MgO are important factors that can affect a slag viscosity and melting temperature, and have been widely studied for various slag systems [13–17]. He [18] studied for effect of MgO on viscosity of blast furnace slag and showed that the slag viscosity decreased with the increasing of MgO content in a definite range, and it decreased obviously with the increasing of slag basicity. Fan's experiment showed that the melting temperature of slag decreased with the increasing of MgO content in slag [16]. However, effects of basicity and MgO in many previous researches are of blast furnace slag [14,19]. The effects of basicity and MgO for vanadium titanomagnetite ore in the electric furnace smelting process are not fully understood, especially the effect of MgO in titanium slag.

In the present study, effects of basicity and MgO content of titanium slag on reduction behaviors of vanadium oxides and titanium oxides, as well as the separation behaviors of titanium slag from iron in smelting vanadium titanomagnetite ore by the direct reduction-electric furnace process were investigated. Different contents of CaO and MgO were added when smelting vanadium titanomagnetite by electric furnace. The vanadium-bearing iron and titanium slag were analyzed and detected by XRF and XRD. The recovery rates of Fe, V were calculated and Ti grades in iron were detected to display the effects of basicity and MgO on reduction of iron oxides, vanadium oxides and titanium oxides. In addition, separation behaviors of titanium slag from iron were analyzed through the pictures of iron and titanium slag and yield of metallized iron in magnetic separation. At last, these findings will provide the technological basis for commercial utilization of vanadium titanomagnetite ore by the direct reduction-electric furnace process in China.

2. Materials and Experimental

2.1. Materials

The vanadium titanomagnetite concentrate used in this investigation was provided by the Chongqing Iron and Steel Company (Sichuan, China). The direct reduction metallized pellet was produced from vanadium titanomagnetite concentrate pellet by coal-based direct reduction in a rotary kiln (\emptyset 1000 mm \times 550 mm, produced by Central South University, Changsha, China).

The main chemical composition of metallized pellet (diameter range 10-15 mm) is listed in Table 1. It shows the metallization rate (=MFe/TFe \times 100%) of pellet is 90.45%. The metallized pellet contained 15.53 wt. % of titanium dioxide and 0.82 wt. % of vanadium oxide. Graphite was used in this research as the reductant. All chemicals and reagents used in this study were of analytical grade.

Table 1. Chemical compositions of metallized pellet (wt. %).

TFe	MFe	CaO	SiO ₂	MgO	Al ₂ O ₃	V_2O_5	TiO ₂	С	S
71.38	64.56	1.01	3.71	2.58	3.83	0.82	15.53	0.036	0.027

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The X-ray diffraction (XRD) pattern of metallized pellets is shown in Figure 1. The major phases in the metallized pellet are metallic iron (Fe), ferrous-pseudobrookite (Fe_{1-x}Mg_xTi₂O₅, $0 \le x \le 1$) and magnesia-alumina spinel (Mg(AlSi₃O₈)), respectively.

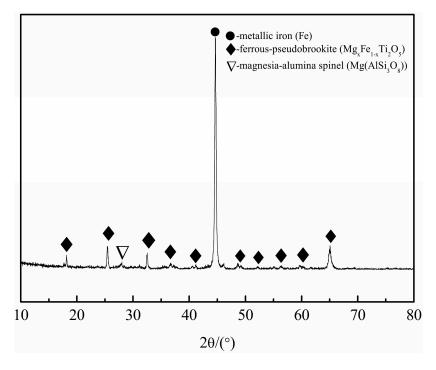


Figure 1. XRD pattern of metallized pellet.

2.2. Thermodynamics Analysis Methods

FactSage 7.0 (Thermfact/CRCT, Montreal, QC, Canada; GTT-Technologies, Herzogenrath, Germany) was used to draw the phase diagram and calculate the liquid temperature and viscosity of simulated titanium slag in this study [20]. The used modules were "Reaction", "Equlib", "Phase Diagram", "Viscosity", and the corresponding database was "FToxid".

2.3. Experimental Procedure

The high-temperature electric furnace (model: SG-160-MoSi₂, The Great Wall Furnace, Changsha, China) was used to smelt vanadium titanomagnetite ore (Figure 2). The metallized pellets were crushed at first (<1 mm), then mixed with additives (CaO, MgO) and graphite together. The well-mixed samples (200 grams) were placed in the graphite crucible ($\varnothing 50 \times 100$ mm) after the target temperature was reached and they were reduced in the high-temperature laboratory furnace at various temperatures with the protection of Ar. After smelting time was up, the crucible was taken out and cooled in neutral condition with Ar. Finally, the vanadium-bearing iron and titanium slag were crushed and detected by XRF and XRD.

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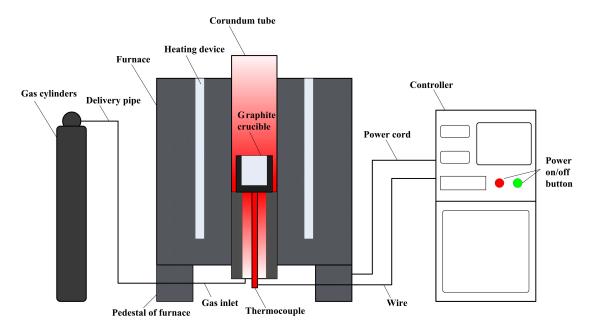


Figure 2. The SG-160-MoSi₂ furnace in the laboratory.

2.4. Definition of Parameters

2.4.1. Basicity

The basicity in this paper was quaternary basicity, which is represented as Equation (1):

$$R = \frac{\text{wt}(\text{CaO}) + \text{wt}(\text{MgO})}{\text{wt}(\text{Al}_2\text{O}_3) + \text{wt}(\text{SiO}_2)}$$
(1)

2.4.2. Recovery Rates

The recovery rates of Fe and V were calculated by Equation (2):

$$\varphi(\text{Fe/V}) = \frac{\text{wt}(\text{Fe/V})_{\text{iron}} \times \text{mass(iron)}}{\text{wt}(\text{Fe/V})_{\text{pellet}} \times \text{mass(pellet)}} \times 100\%$$
 (2)

The reduction behaviors of iron oxides and vanadium oxides were evaluated by the recovery rates of Fe and V, while the reduction behaviors of titanium oxides were evaluated by the Ti grade in iron.

The separation behaviors of titanium slag from iron were evaluated by observing the macroscopic pictures of iron and titanium slag. As residual metallized iron is the only magnetic material in titanium slag after the reduction, the residual metallized iron in titanium slag were separated by magnetic separation with the magnetic field intensity of 0.1 T. Thus, the yield of residual metallized iron in slag was another evaluation index of the separation of iron and titanium slag.

2.5. Analysis of Samples

The chemical composition of the vanadium-bearing iron and titanium slag were measured by X-ray fluorescence spectroscopy (XRF) (PANalytical Axios mAX, PANalytical B.V., Almelo, The Netherlands).

The chemical composition of metallized pellet was analyzed by Chinese standard YB/T 4170-2008. The main phases of metallized pellet and titanium slag were analyzed by X-ray diffraction (XRD) (Cu K α radiation, λ = 1.54056 Å, D/Max2200, Rigaku, Japan).

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3. Experimental Fundamental Thermodynamics

Iron and vanadium are reduced into molten iron and titanium is kept as titanium slag in the direct reduction-electric furnace process. Therefore, the reductions of iron and vanadium were improved and the reduction of titanium was inhibited during the reduction in order to control the smelting direction of Fe, V, and Ti.

Equation (3) shows that the reduction of vanadium starts at a low temperature and is easier at high temperature due to the small value of ΔG_T^{θ} [21]:

$$VO + C = [V] + CO \Delta G_T^{\theta} = 287.247 - 0.208T$$
 (3)

In addition, reduction of titanium oxides was controlled to limit the amount of titanium carbides in slag. The development of titanium carbides in slag increases the viscosity of slag and prevent separation of iron from titanium slag [22]. Thus, titanium oxides which are difficult to reduce to TiC were found in order to decrease the appearance of TiC in slag.

The reduction reactions of possible titanium oxides in smelting process according to the composition of metallized pellet were calculated by FactSage 7.0. Equations (4)–(7) shows that the reduction temperatures to TiC of MgTi₂O₅, Al₂TiO₅, CaTiO₃, and CaSiTiO₅ are 1629.77 K, 1590.26 K, 1863.16 K, 1709.16 K, respectively. It indicates that MgTi₂O₅, CaTiO₃, and CaSiTiO₅ have high reaction temperatures, however, Al₂TiO₅ is easier to be reduced to TiC due to its lower reduction temperature.

$$MgTi_2O_5 + 6C = MgO + 2TiC + 4CO \quad \Delta G_T^{\theta} = 1059.35 - 0.650T$$
 (4)

$$Al_2TiO_5 + 3C = Al_2O_3 + TiC + 2CO \quad \Delta G_T^{\theta} = 478.668 - 0.301T$$
 (5)

$$CaTiO_3 + 3C = CaO + TiC + 2CO \quad \Delta G_T^{\theta} = 603.663 - 0.324T$$
 (6)

CaSiTiO₅ + 3C = CaSiO₃ + TiC + 2CO
$$\Delta G_T^{\theta} = 500.784 - 0.293T$$
 (7)

Furthermore, the TiO_2 in titanium slag should increase to about 50% to ensure the recovery of titanium from slag by the acid leaching method. Therefore, the calculated TiO_2 content of titanium oxides, in the order from high to low, is shown:

$$MgTi_{2}O_{5}\left(76.2\%\right) \, > \, CaTiO_{3}\left(58.8\%\right) \, > \, Al_{2}TiO_{5}\left(43.96\%\right) \, > \, CaSiTiO_{5}\left(40.8\%\right)$$

It is clearly seen that, even though $CaSiTiO_5$ has a higher reduction temperature, but it should not as the target mineral due to its low titanium content. The Al_2TiO_5 was inappropriate to be chosen due to the same reason, and the content of SiO_2 was kept constant due to the addition of SiO_2 decreased TiO_2 content of titanium slag. As a result, the $MgTi_2O_5$ and $CaTiO_3$ were suitable minerals in titanium slag, and the effects of CaO and MgO in slag needed to be investigated.

The separation of iron and titanium slag during the electric furnace process requires both low-viscosity slag and low melting temperature conditions. In this study, related phase diagrams were analyzed to identify the optimum compositions of slag suited to low melting temperature. The main chemical compositions of the metallized pellet are TiO_2 , CaO, SiO_2 , MgO, and Al_2O_3 ; the phase diagram of CaO- SiO_2 -MgO- TiO_2 - Al_2O_3 (Figure 3) was accordingly drawn and analyzed, with special focus on keeping the two compositions in the phase diagram constant. The content of TiO_2 was maintained at 50% constant, because analysis indicated that this amount of TiO_2 titanium slag can be used to recover Ti via the sulfuric acid process; Al_2O_3 content was kept constant at 13%. The optimum range of MgO content and suitable basicity in the titanium slag were identified according to the isothermal section of phase diagram (Figure 3) at 1400 $^{\circ}C$ of CaO- SiO_2 -MgO- TiO_2 (50%)- Al_2O_3 (13%) drawn in FactSage 7.0. The red area in this phase diagram, *i.e.*, the melting temperature below 1400 $^{\circ}C$.

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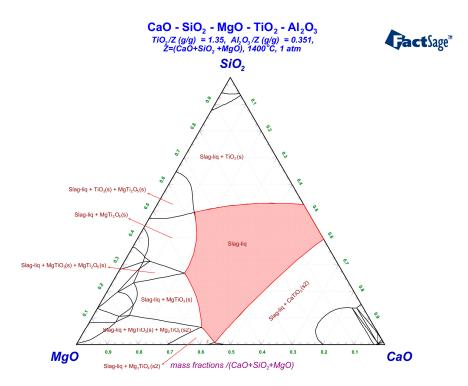


Figure 3. Isothermal section of phase diagram of CaO-SiO₂-MgO-TiO₂ (50%)-Al₂O₃ (13%) at 1400 °C.

Optimum contents of CaO, SiO_2 , and MgO in titanium slag were determined as 8%–20%, 8%–18%, and 6%–14%, respectively, through careful analysis of the phase diagram. To investigate the effects of basicity and MgO content on melting temperatures, different binary basicity levels, MgO contents and the corresponding melting temperatures were also calculated by FactSage 7.0.

Figure 4 shows the changes of melting temperatures with different binary basicity and MgO contents, where we found that the melting temperature decreased as MgO content increased and decreased at first, then gradually increased with the increasing binary basicity. The suitable binary basicity range was 0.8–1.2 and MgO content was approximately 8%–12% within the appropriate temperature range.

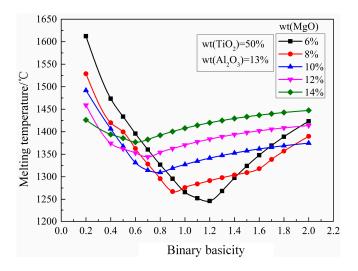


Figure 4. Effects of binary basicity and MgO content on melting temperature (FactSage 7.0).

Viscosity is one of the important physiochemical properties of slags in high-temperature extractive metallurgy [13]; generally, low slag viscosity promotes effective separation. The viscosity of titanium

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slag with different quaternary basicity was investigated by adjusting different CaO and MgO contents in FactSage 7.0 as shown in Figures 5 and 6.

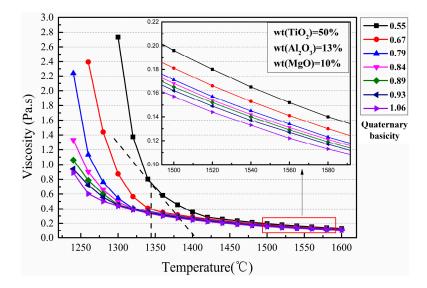


Figure 5. Effects of quaternary basicity by addition of CaO on titanium slag viscosity (FactSage 7.0).

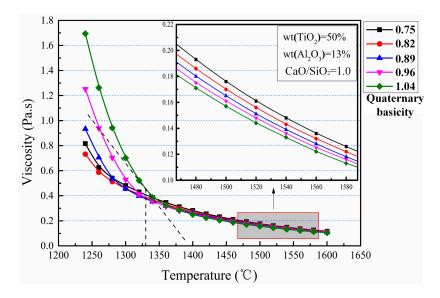


Figure 6. Effects of quaternary basicity by addition of MgO on titanium slag viscosity (FactSage 7.0).

The quaternary basicity was changed by adjusting content of CaO with constant MgO content in Figure 5, in contrast, MgO content was changed with constant CaO/SiO₂ to change the quaternary basicity in Figure 6. Figure 5 shows where the viscosity of the titanium slag decreases as its quaternary basicity increases, and the expanded image in Figure 6 indicates that the viscosity of titanium slag decreases as MgO content increases. Previous studies have also reported that the addition of MgO decreases slag viscosity [14,18]. In effect, addition of CaO and MgO to increase quaternary basicity can decrease the viscosity of titanium slag and promote the optimal separation of iron and slag.

Free running temperature is also a critical factor affecting slag properties. It is defined as the lowest temperature at which the slag becomes liquid and, as the term suggests, flow freely. In this study, the free running temperatures were defined according to the viscosity-temperature curves (Figures 5 and 6) as shown in Figure 7a,b: our method for doing so involved drawing a tangent line at 45 degree angle to the *X* axis, where the temperature of the tangent point on the curve is the free running

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temperature of the slag [21]. Figure 7 shows where increasing quaternary basicity by addition of CaO decreases the free running temperature until reaching a threshold at about 0.95 basicity, at which free running temperature increases. Free running temperature increases as quaternary basicity increases by addition of MgO.

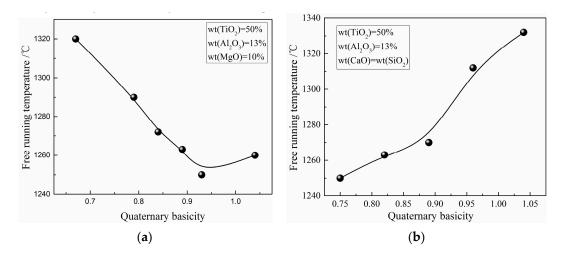


Figure 7. (a) Effects of quaternary basicity by addition of CaO content on free-running slag temperature; and (b) effects of quaternary basicity by addition of MgO content on free-running slag temperature.

Briefly, our thermodynamic analysis of the titanium slag indicated that the suitable quaternary basicity range is 0.9–1.2 and that MgO addition decreases titanium slag viscosity but increases its melting temperature and free-running temperature. Accordingly, the effects of quaternary basicity (0.9–1.2) and MgO content (8%–14%) were the focus of our subsequent investigation.

4. Results and Discussion

In this study, effects of quaternary basicity and MgO content in slag were investigated through adding different contents of CaO and MgO, and contents of Al_2O_3 and SiO_2 were not changed. Table 2 shows the design of experiments and the smelting parameters.

No.	Binary Basicity	Quaternary Basicity	MgO/%	Smelting Temperature/°C	Smelting Time/min	Reducing Agent/%
1	0.8	0.98	11.38	1550	20	2
2	0.9	0.99	11.38	1550	20	2
3	1.0	1.04	11.38	1550	20	2
4	1.1	1.10	11.38	1550	20	2
5	1.2	1.16	11.38	1550	20	2
6	1.1	0.88	7.97	1550	20	2
7	1.1	0.96	9.79	1550	20	2
8	1.1	1.13	12.75	1550	20	2
9	1.1	1.10	11.38	1550	20	5

Table 2. Titanium slag composition and smelting parameters.

4.1. Effects of Basicity

The effects of quaternary basicity on the smelting of vanadium titanomagnetite ore were investigated by varying the quaternary basicity level by addition of CaO under the following conditions (No. 1–No. 5): constant MgO content (11.38%), smelting temperature (1550 $^{\circ}$ C) and smelting time (20 min) with 2% reducing agent. Figure 8 shows that lower basicity levels with constant MgO content had significant effect on the recovery rates of Fe and V, as well as the Ti grade in the iron. As showed in

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Figure 8a, the recovery rates of Fe and V increased as basicity increased, indicating that higher level of basicity benefits the reduction of iron oxides and vanadium oxides. Figure 8b indicates that titanium content dropped as iron decreased with the increasing quaternary basicity. In short, the results show that the basicity must be kept above 1.0 to ensure favorable results.

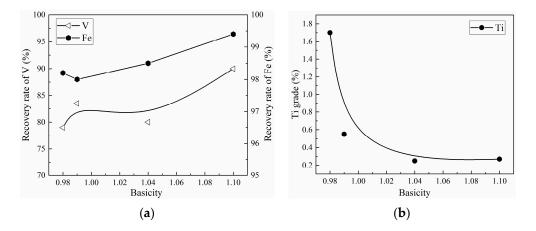


Figure 8. (a) Effects of quaternary basicity by addition of CaO on Fe and V recovery rates; and (b) effects of quaternary basicity by addition of CaO on Ti grade in iron.

The XRD pattern shown in Figure 9 demonstrates that the main phase compositions in the samples were perovskite (CaTiO₃), anosovite (MgTi₂O₅), and magnesium-aluminum silicate (Mg₃Al₂CaSi₂O₆). As basicity increased, the content of MgTi₂O₅ decreased while the contents of CaTiO₃ and Mg₃Al₂CaSi₂O₆ increased. Further, the results of thermodynamic analysis (Equations (4) and (6)) suggested that, increases in CaTiO₃ and decrease in MgTi₂O₅ inhibit the thermodynamic trend of titanium reducing to iron, and cause the Ti grade in the iron to decrease (Figure 8b). Moreover, the appearance of TiC particles in the titanium slag is known to raise its viscosity [22], hence the increasing CaTiO₃ having decreased the reduction trend to TiC in the titanium slag. Excessive basicity, however, increased the melting temperature because CaTiO₃ is a high-melting-point material.

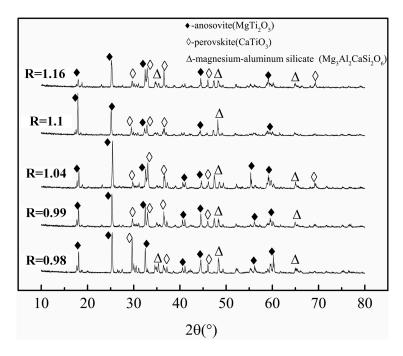


Figure 9. XRD patterns of titanium slag with different quaternary basicity levels by addition of CaO.

Figure 10 shows macroscopical pictures of the separation of iron and titanium slag with different basicity conditions; the iron is marked by the red line and the titanium slag is marked by the green line. Clearly, the separation was incomplete at a basicity of 0.98 as evidenced by the numerous iron shots (red circles) in the titanium slag. There were also several iron shots in the slag at a basicity of 1.04. Separation was optimal at a basicity of 1.10, where there were the fewest iron shots. Figure 11 shows the yield of residual iron in magnetic separation decreases firstly as basicity increases, then increases when basicity above 1.10. In short, our analysis of the effects of basicity on Fe, V, and Ti separation behaviors in iron and titanium slag indicated that the optimum quaternary basicity is about 1.10.

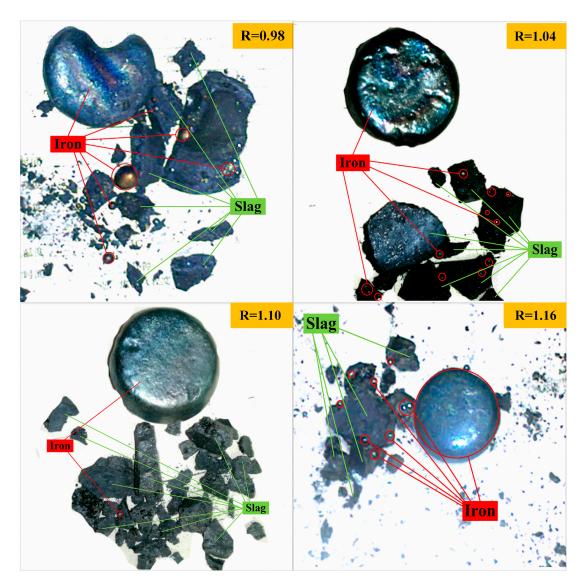


Figure 10. Pictures of iron and titanium slag separation with varying quaternary basicity by addition of CaO.

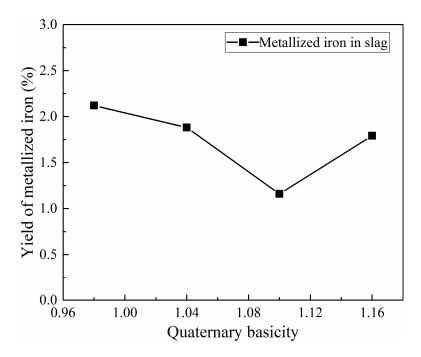


Figure 11. Effects of quaternary basicity by addition of CaO on yield of residual metallized iron in slag.

4.2. Effects of MgO

The effects of MgO on the smelting process were studied in the mass range of 7.97% to 12.75% with constant CaO. Figure 12 shows that as the content of MgO increased, the recovery rate of Fe increased slightly and the recovery rate of V increased considerably. It can be inferred that the grades of Ti in molten iron were at a low level and did not change significantly at MgO content below 11%, but increased as MgO content increased to 12.75%. Basically, increasing MgO content in the slag is beneficial, but only within a suitable range; otherwise, the reduction of titanium oxide will increase.

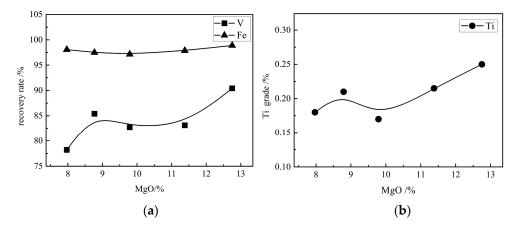


Figure 12. (a) Effects of MgO on Fe and V recovery rates; and (b) effects of MgO on the Ti grade in iron.

The XRD pattern shown in Figure 13 demonstrates that main phase compositions were CaTiO₃, MgTi₂O₅, and Mg₃Al₂CaSi₂O₆. As MgO content increased, the content of MgTi₂O₅ likewise increased, while the contents of CaTiO₃ and Mg₃Al₂CaSi₂O₆ decreased. Again, based on thermodynamic analysis (Equations (4) and (6)) of titanium oxide reduction, the thermodynamic tendency of the reduction from MgTi₂O₅ to TiC occurs more readily than that of CaTiO₃, so as MgO content increased beyond 12.75%, the Ti grade in the iron increased. Previous research has also indicated that Ti-bearing blast furnace slag viscosity increases as the perovskite phase increases [23], so reduction in titanium slag

viscosity facilitates the reduced diffusion of Fe and V. The same thermodynamic analysis mentioned above also suggests that decrease in $CaTiO_3$ and increase in $MgTi_2O_5$ increase the thermodynamic trend of titanium reducing to iron and increase the Ti grade in iron (Figure 12b).

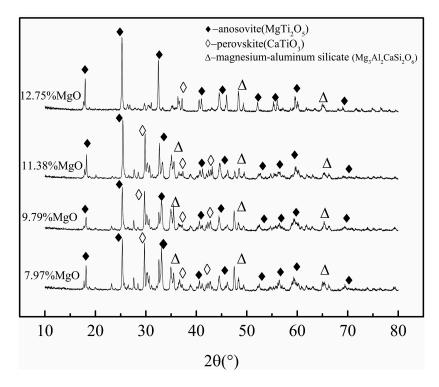


Figure 13. XRD patterns of titanium slag with varying MgO content.

The separation pictures of iron and titanium slag with varying MgO content are shown in Figure 14. Clearly, different MgO contents had different effects on separation. When MgO content was 7.97%, the separation was not optimal (*i.e.*, there were iron shots in the titanium slag), and when the MgO content increased to 12.75%, iron and titanium slag mixed together and the separation of iron and slag was again incomplete. Separation was better as MgO content increased from 9.79% to 11.38%, as the degree of polymerization among Si–O and Al–O decreased as MgO content increased; as the O²⁻ ions were impacted by the addition of MgO, the network structures of their formation were destroyed and transformed into simple single- and double-tetrahedron structures [21]. Thus, MgO reduced slag viscosity and promoted aggregation and settlement of molten iron, ultimately favoring the separation of iron and titanium slag. Figure 15 shows the yield of residual metallized iron in magnetic separation decreased gradually as MgO content increased. In short, it shows where about 11.38% MgO was optimal for the effective separation of iron and titanium slag.

In summary, the optimum quaternary basicity and MgO content were 1.10 and 11.38%, the vanadium-bearing iron and titanium slag were produced under the following conditions (No. 8): smelting at $1550\,^{\circ}$ C and 20 min, the reducing agent is 5%. Tables 3 and 4 show the main elements in iron and the main compositions of titanium slag. The recovery rates of Fe and V were 99.59% and 95.52%, respectively, and the titanium slag contained $50.34\%\,\text{TiO}_2$. The vanadium-bearing iron can be applied to recover iron and vanadium by the converter steelmaking process, and the titanium slag can be used to recover titanium by the acid leaching method [1,24].

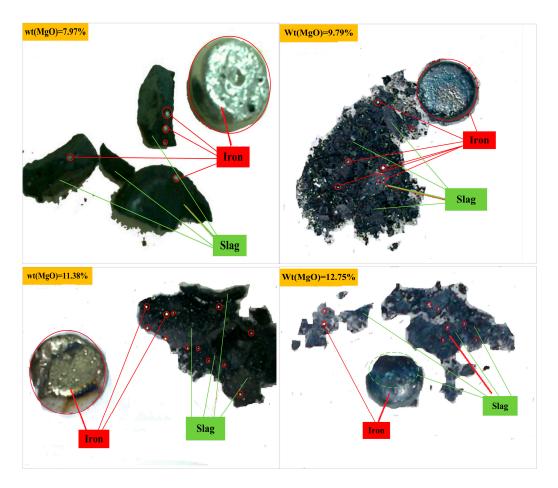


Figure 14. Separation photos of iron and slag with varying MgO content.

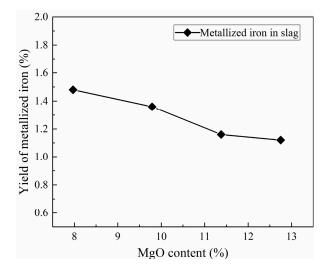


Figure 15. Effect of MgO content on yield of residual metallized iron in slag.

Table 3. Production index of vanadium-bearing iron.

Eleme	ent Grade	Recovery Rate/%			
TFe	V	Si	Ti	V	Fe
98.09	0.683	0.199	0.296	95.52	99.59

Table 4. Main composition of titanium slag (wt. %).

TiO ₂	V_2O_5	TFe	Al ₂ O ₃	MgO	CaO	SiO ₂
50.34	0.162	1.051	13.05	11.38	11.79	11.68

5. Conclusions

Effects of basicity and MgO content on reduction behaviors and iron-slag separation during smelting vanadium titanomagnetite ore by the direct reduction-electric furnace process were investigated in this paper.

- (1). The related thermodynamic analysis indicated that the suitable basicity range was 0.9–1.2. The addition of MgO decreased titanium slag viscosity but increased its melting temperature and free-running temperature.
- (2). A higher level of basicity benefits the reduction of iron oxides and vanadium oxides, and titanium content dropped in molten iron with the increased basicity. The optimum basicity was about 1.1. As the content of MgO increased, the recovery rate of Fe increased slightly, but the recovery rate of V considerably increased. The grades of Ti in molten iron were at a low level without significant change when MgO content was below 11%, but increased as MgO content increased to 12.75%. MgO content of 11.38% and basicity of 1.1 were the optimum conditions in this study.
- (3). The vanadium-bearing iron and titanium slag were produced at 1550 °C and 20 min, with 5% reducing agent. The recovery rates of Fe and V were 99.59% and 95.52%, respectively. The titanium slag contained 50.34% TiO₂. The vanadium-bearing iron can be applied in the converter steelmaking process and titanium slag can be utilized by the acid leaching method.

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References

- 1. Zheng, F.Q.; Chen, F.; Guo, Y.F.; Jiang, T.; Travyanov, A.Y.; Qiu, G.Z. Kinetics of Hydrochloric Acid Leaching of Titanium from Titanium-Bearing Electric Furnace Slag. *JOM* **2016**, *68*, 1476–1484. [CrossRef]
- 2. Taylor, P.R.; Shuey, S.A.; Vidal, E.E.; Gomez, J.C. Extractive metallurgy of vanadium-containing titaniferous magnetite ores: A review. *Miner. Metall. Proc.* **2006**, *23*, 80–86.
- 3. Du, H.G. *Principle of Blast Furnaces Melting Vanadium-Titanium Magnetite*; Science Press: Beijing, China, 1996; pp. 6–8.
- 4. Tan, Q.Y.; Chen, B.; Zhang, Y.S.; Long, Y.B.; Yang, Y.H. Characteristics and Current Situation of Comprehensive Utilization of Vanadium Titanomagnetite Resources in Panxi Region (In Chinese). *Multipurp. Util. Miner. Resour.* 2011, 6, 6–10.
- 5. Chen, S.Y.; Chu, M.S. A new process for the recovery of iron, vanadium, and titanium from vanadium titanomagnetite. *J. South. Afr. Inst. Min. Metall.* **2014**, *114*, 481–488.
- 6. Samanta, S.; Mukherjee, S.; Dey, R. Upgrading Metals via Direct Reduction from Poly-metallic Titaniferous Magnetite Ore. *JOM* **2015**, *67*, 467–476. [CrossRef]
- 7. Fu, W.G.; Wen, Y.C.; Xie, H.E. Development of intensified technologies of vanadium-bearing titanomagnetite smelting. *J. Iron Steel Res. Int.* **2011**, *18*, 7–18. [CrossRef]
- 8. Liu, X.J.; Chen, D.S.; Chu, J.L.; Wang, W.J.; Li, Y.L.; Qi, T. Recovery of titanium and vanadium from titanium–vanadium slag obtained by direct reduction of titanomagnetite concentrates. *Rare Met.* **2015**. [CrossRef]

9. Guo, Y.F. Study on Strenthening of Solid-State Reduction and Comprehensive Utilization of Vanadiferous Titanomagnetite (In Chinese). Ph.D. Thesis, Central South University, Changsha, China, July, 2007.

- 10. Jones, J.A.; Bowman, B.; Lefrank, P.A. Electric Furnace Steelmaking. Available online: http://jpkc.gsut.edu.cn/upload/20120523/20120523181249992.pdf (accessed on 6 May 2016).
- 11. Tang, J.; Chu, M.; Xue, X. Optimized use of MgO flux in the agglomeration of high-chromium vanadium-titanium magnetite. *Int. J. Miner. Metall. Mater.* **2015**, *22*, 371–380. [CrossRef]
- 12. Liu, Z.; Chu, M.; Wang, H.; Zhao, W.; Xue, X. Effect of MgO content in sinter on the softening-melting behavior of mixed burden made from chromium-bearing vanadium-titanium magnetite. *Int. J. Miner. Metall. Mater.* **2016**, 23, 25–32. [CrossRef]
- 13. Chen, M.; Raghunath, S.; Zhao, B. Viscosity Measurements of SiO₂-"FeO"-MgO System in Equilibrium with Metallic Fe. *Metall. Mater. Trans. B* **2014**, *45*, 58–65. [CrossRef]
- 14. Gao, Y.; Wang, S.; Hong, C.; Ma, X.; Yang, F. Effects of basicity and MgO content on the viscosity of the SiO₂-CaO-MgO-9wt%Al₂O₃ slag system. *Int. J. Miner. Metall. Mater.* **2014**, *21*, 353–362. [CrossRef]
- 15. Li, P.; Ning, X. Effects of MgO/Al₂O₃ Ratio and Basicity on the Viscosities of CaO-MgO-SiO₂-Al₂O₃ Slags: Experiments and Modeling. *Metall. Mater. Trans. B* **2016**, 47, 446–457.
- 16. Fan, J.J.; Cai, M.X.; Zhang, H. Study on effects of Al₂O₃ content and MgO content on melting temperature at BF slag (In Chinese). *Shanxi Metall.* **2007**, *30*, 22–23.
- 17. Shankar, A.; Rnerup, M.R.G.; Lahiri, A.K.; Seetharaman, S. Experimental Investigation of the Viscosities in CaO-SiO₂-MgO-Al₂O₃ and CaO-SiO₂-MgO-Al₂O₃-TiO₂ Slags. *Metall. Mater. Trans. B* **2007**, *38*, 911–915. [CrossRef]
- 18. He, H.Y.; Wang, Q.X.; Zeng, X.N. Effect of MgO content on BF slag viscosity (In Chinese). *J. Iron Steel Res.* **2006**, *18*, 11–13.
- 19. Li, J.; Zhang, Z.; Liu, L.; Wang, W.; Wang, X. Influence of Basicity and TiO₂ Content on the Precipitation Behavior of the Ti-bearing Blast Furnace Slags. *ISIJ Int.* **2013**, *53*, 1696–1703. [CrossRef]
- Bale, C.W.; Bélisle, E.; Chartrand, P.; Decterov, S.A.; Eriksson, G.; Hack, K.; Jung, I.H.; Kang, Y.B.; Melançon, J.; Pelton, A.D.; et al. FactSage thermochemical software and databases—Recent developments. Calphad 2009, 33, 295–311. [CrossRef]
- 21. Huang, X.H. Principles of Iron and Steel Metallurgy; Metallurgy Industry Press: Beijing, China, 2013; pp. 60–440.
- 22. Zhen, Y.; Zhang, G.; Chou, K. Viscosity of CaO-MgO-Al₂O₃-SiO₂-TiO₂ Melts Containing TiC Particles. *Metall. Mater. Trans. B* **2015**, 46, 155–161. [CrossRef]
- Zhang, L.; Zhang, L.N.; Wang, M.Y.; Lou, T.P.; Sui, Z.T.; Jang, J.S. Effect of perovskite phase precipitation on viscosity of Ti-bearing blast furnace slag under the dynamic oxidation condition. *J. Non-Cryst. Solids* 2006, 352, 123–129. [CrossRef]
- 24. Yang, S.L. *Non-Blast Furnace Smelting Technology for Vanadium Titanomagnetite Ore*; Metallurgy Industry Press: Beijing, China, 2012.



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