

Reduction Behaviors of Iron, Vanadium and Titanium Oxides in Smelting of Vanadium Titanomagnetite Metallized Pellets

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The complicated reduction behaviors of iron, vanadium and titanium oxides must be accurately controlled for the successful smelting of vanadium titanomagnetite. The aim of this study is to investigate the effects of the binary basicity, MgO content, smelting temperature, duration and reductants on the reduction of iron, vanadium and titanium oxides during the electric furnace smelting of vanadium titanomagnetite metallized pellets. The results demonstrate that the recovery ratios of both iron and vanadium increase as the binary basicity increases from 0.9 to 1.2, whereas the reduction of titanium oxides is mitigated when the basicity is maintained at 1.1. Compared to its weak effect on the recovery ratio of iron, increasing MgO content improves the vanadium recovery ratio. A low content of titanium in molten iron is obtained when the MgO content in the slag is lower than 11%, whereas the titanium content in the molten iron increases as the MgO content increases further. Moreover, the iron and vanadium recovery ratios, and the Ti content in the molten iron, increase with increasing smelting temperature, duration and reductant content.

INTRODUCTION

Vanadium titanomagnetite is a complex iron ore which contains iron, vanadium, titanium and other rare metal elements.^{1,2} The vanadium titanomagnetite resources are abundant in the Panxi region of China, where the reserves are approximately 9.66 billion tons.³ The titanium resource in this region accounts for approximately 95% of Chinese total reserves, and approximately 54% of the titanium resource becomes the vanadium titanomagnetite concentrate after physical separation.^{1,3} Therefore, it is crucial to recover titanium from the vanadium titanomagnetite concentrate. A traditional blast furnace process has been utilized for these resources in China and Russia.^{4,5} The coke is utilized as both the fuel and reductant in the blast furnace process, which causes an excessive reduction potential in the hearth and difficult control of reduction of the vanadium and titanium oxides during the blast furnace smelting.³ In addition, the Ti(C,N) is easily formed during the vanadium titanomagnetite smelting, whereas the Ti(C,N) particles generated

cause an increase of the titanium slag viscosity and difficult separation of the iron from the slag.^{1,3} For reduction of Ti(C,N), ordinary iron ores are mixed with the vanadium titanomagnetite concentrate in order to reduce the TiO₂ content in the titanium slag during the blast furnace smelting. As a result, the blast furnace titanium slag contains only 20–25 wt.% of TiO₂, which cannot be effectively recovered, leading to serious environmental pollution.^{4,5} For comprehensive utilization of vanadium titanomagnetite ore, many methods have been developed or are under development, such as the direct reduction–electric furnace smelting and direct reduction–magnetic separation.^{1,3,6–12} In addition, the direct reduction–electric furnace process has been commercialized in South Africa and New Zealand with environmental friendliness, large capacity and stable quality of the products.²

Compared to the blast furnace process, the direct reduction–electric furnace process is proven to be beneficial for the control of reduction of vanadium and titanium oxides due to the metallized pellets heated by electrodes.³ In the direct reduction–

electric furnace process, both the iron and vanadium oxides are reduced into molten iron and the titanium is enriched in the titanium slag. Moreover, the titanium oxides can be excessively reduced to TiC in this process, which increases the viscosity of the titanium slag and causes a difficult separation between the molten iron and the titanium slag.¹³ Therefore, the reduction directions of the vanadium and titanium oxides must be controlled during smelting for a successful separation between the iron and slag. In South Africa, dolomite and quartz were added to control the slag composition for mitigation of the excessive titanium reduction.¹⁴ As a result, the TiO₂ content was reduced in the slag and a titanium slag with 30–33 wt.% of TiO₂ was obtained. Unfortunately, the titanium resource in the titanium slag cannot be effectively or economically recovered due to its low TiO₂ content.

To increase the recovery ratio of titanium, titanium slag with a higher TiO₂ content should be produced. Previous studies indicated that the titanium resource could be easily recovered by the acid leaching method on an industrial scale if the titanium slag contained a higher TiO₂ content.³ Roshcin¹⁵ investigated the solid-phase reduction of titaniferous magnetite concentrates and the smelting of the reduction products. The titanium in the obtained cast iron was less than 0.85 wt.%, whereas the titanium slag contained approximately 43 wt.% TiO₂. Wang¹⁶ obtained a slag with 46.8 wt.% TiO₂ after smelting at 1500°C for 2 h at a basicity of 1.4. Also, according to Wu,¹⁷ the suitable basicity (CaO/SiO₂) was 0.6 and the carbon addition should be lower than 5% for production of the slag with over 47 wt.% TiO₂. However, the reduction behaviors of iron, vanadium and titanium oxides during the electric furnace smelting process were not clear. In addition, many previous studies have been focused on the blast furnace smelting of vanadium titanomagnetite.^{18–20} Therefore, it is necessary to investigate the reduction behaviors of iron, vanadium and titanium oxides for the utilization of the vanadium titanomagnetite available in China.

The aim of the present study is to study the reduction behaviors of iron, vanadium and titanium oxides during vanadium titanomagnetite smelting in an electric furnace. The thermodynamic reduction reactions were systematically calculated and analyzed by the FactSage 7.0 software. The slag compositions and smelting parameters were adjusted for promoting the reduction of iron oxides and vanadium oxides and for suppressing the reduction of the titanium oxides. Moreover, the electric furnace experiments were performed to examine the effects of the slag binary basicity, the MgO content in the slag, the smelting temperature, the duration and the reductant content. The findings are useful for the effective recovery of the Fe, V and Ti oxides from vanadium titanomagnetite.

EXPERIMENTAL PROCEDURE

Materials

The vanadium titanomagnetite concentrate used in this study was taken from the Taihe iron ore in the Panxi region of China. The metallized pellet was produced from the vanadium titanomagnetite concentrate pellet by the coal-based direct reduction in a rotary kiln at 1100°C with a C/Fe ratio of 1:1 for 3 h. The main chemical composition of the metallized pellet is summarized in Table I. The reductant was powdered graphite. All chemicals and reagents utilized in the experiments were of analytical grade.

The mineralogical analysis of the samples was investigated by x-ray diffraction (XRD). The result indicated that the main crystalline phases of the metallized pellets were metallic iron (Fe), ferrous-pseudobrookite (Fe_{1-x}Mg_xTi₂O₅, 0 ≤ x ≤ 1) and magnesia–alumina spinel.²¹

Experimental Apparatus

The experiments were conducted in an electric furnace with a MoSi₂ heating element. The schematic diagram was illustrated in the authors' previous paper.²¹ The experimental procedure is described as follows. First, the metallized pellets were crushed (<1 mm), and then mixed with given amounts of additives (CaO, MgO) and graphite powder using an agate mortar. The well-mixed sample (200 g) was placed in a graphite crucible (inner diameter 50 mm, height 100 mm) and raised to the hot zone of the electric furnace and smelted at specified temperatures for desirable periods of time under the protection of argon gas (≥99.99%). The gas flow rate was monitored by a mass flow controller and the flow rate was 3 L/min. At the end of smelting period, the samples were quickly removed from the furnace and rapidly cooled under the protection of high-purity argon gas. The slag and metal samples were carefully separated from the crucible and the samples were used for analysis of their chemical compositions.

Definition of Parameters

The recovery ratios of the iron and vanadium were utilized to demonstrate the reduction degree of the iron and vanadium oxides, whereas the Ti content in the molten iron was utilized to demonstrate the titanium oxide reduction.

The recovery ratios of both Fe and V were calculated by the following formula:

$$\varphi(\text{Fe/V}) = \frac{\text{wt}(\text{Fe/V})_{\text{iron}} \times \text{mass}(\text{iron})}{\text{wt}(\text{Fe/V})_{\text{pellet}} \times \text{mass}(\text{pellet})} \times 100\% \quad (1)$$

The binary basicity used in this paper was defined as follows:

$$R = \frac{\text{wt}(\text{CaO})}{\text{wt}(\text{SiO}_2)}. \quad (2)$$

Analysis and Characterization

FactSage 7.0 software was adopted for the thermodynamics analysis of the reduction reactions and the TiO_2 activity in the slag. The utilized modules were “Reaction” and “Equilib”. In addition, the corresponding database was “FToxid”.²² The chemical composition of the titanium slag was analyzed by x-ray fluorescence (PANalytical, The Netherlands). The chemical compositions of the vanadium titanomagnetite concentrate metallized pellet and the Fe, V, Ti grades in the molten iron were analyzed by chemical analysis.

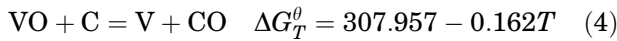
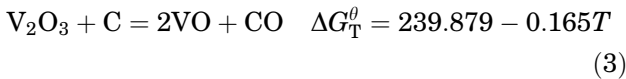
THERMODYNAMIC ANALYSIS

Reduction of Iron Oxides

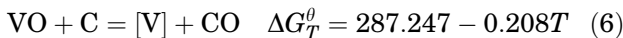
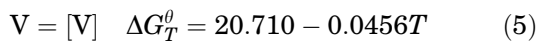
In general, the reduction of iron oxides to metallic iron is relatively easy and the reaction temperature is low.²³ The XRD patterns of the metallized pellets demonstrated that most iron oxides were reduced to metallic iron.

Reduction of Vanadium Oxides

The vanadium in vanadium titanomagnetite ore is the trivalent vanadium (V^{3+}) forming a solid solution with the magnetite lattice in the form of vanadium spinel $[\text{FeO} \cdot (\text{Fe}, \text{V})_2\text{O}_3]$.²⁴ The stepwise reduction of the vanadium oxides is as follows: $\text{FeO} \cdot \text{V}_2\text{O}_3 \rightarrow \text{V}_2\text{O}_3 \rightarrow \text{VO} \rightarrow \text{V} \rightarrow [\text{V}]$.



Equations 3 and 4 demonstrate that VO and V are generated at 1180°C and 1627.9°C, respectively. Upon completion of vanadium oxide reduction, all the vanadium is dissolved into the molten iron.^{24,25} Therefore, the reduction reaction of the vanadium oxides during smelting is expressed by Eq. 6 which was calculated from Eqs. 4 and 5:

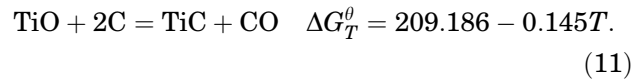
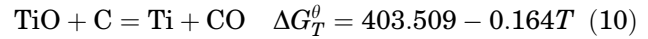
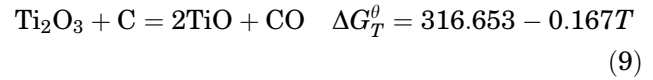
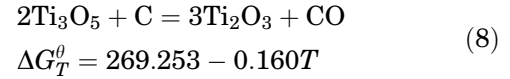
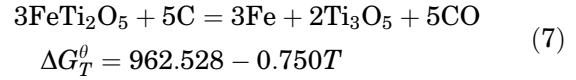


Apparently, compared to Eq. 4, the reaction temperature of Eq. 6 decreased to 1107.9°C. Consequently, the vanadium oxides could be reduced at a low temperature during smelting due to the smaller change of Gibbs free energy.

Reduction of Titanium Oxides

According to the XRD patterns of the metallized pellets, the main phase containing titanium in the metallized pellets was ferrous-pseudobrookite ($\text{Fe}_{1-x}\text{Mg}_x\text{Ti}_2\text{O}_5$, $0 \leq x \leq 1$). Equations 7–11 demonstrate the reduction reactions of the titanium

oxides, whereas the FactSage 7.0 was utilized for the Gibbs free energy changes calculation of these reactions. The results are shown in Fig. 1.



Equations 8–11 demonstrate that the generation temperatures of Ti_2O_3 , TiO, Ti and TiC are 1409.8°C, 1623.1°C, 1787.4°C and 1169.7°C, respectively. It is apparent that the reduction temperatures increase as the titanium valence decreases. In addition, the reaction temperature of TiO to TiC is lower than the others. Meanwhile, titanium carbide (TiC) has a high melting temperature (3150°C). Previous studies indicated that the slag viscosity increased as the TiC in the slag increased.¹⁰ Therefore, it is necessary to control the titanium oxide reduction to reduce the TiC particle amount in the titanium slag.

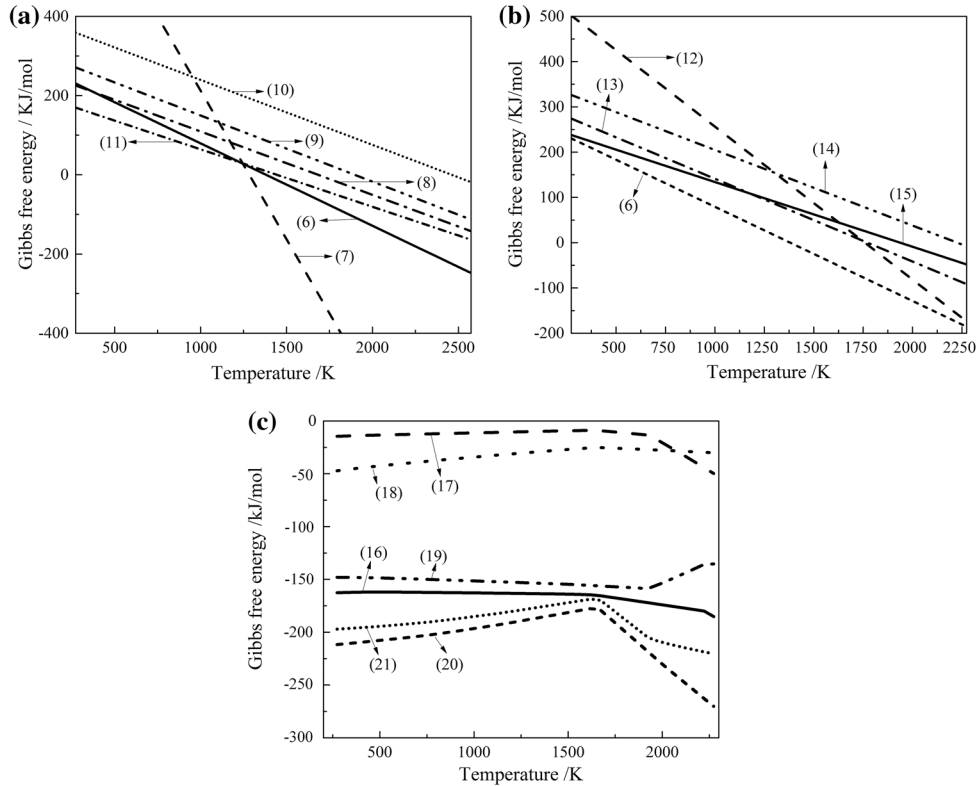
In general, the reduction of titanium oxides by the solid carbon obeys the following gradual reduction principle: $\text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO} \rightarrow \text{TiC}$, where each reduction process is accompanied by a phase change. The Ti_3O_5 is either monoclinic or orthorhombic and the Ti_2O_3 is rhombohedral. Also, both TiO and TiC belong to the cubic system, and the corresponding lattice constants are 0.4162 nm and 0.4329 nm, respectively. Due to the similar crystal structure and almost identical lattice constant, the reduction of TiO to TiC does not induce phase transitions, where the oxygen atoms in the lattice positions are replaced by carbon atoms.²⁶ Therefore, TiC formation becomes easier when TiO is present during smelting. Therefore, the TiO formation must be controlled to reduce the TiC generation in the slag.

Reduction of Titanates

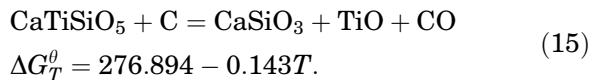
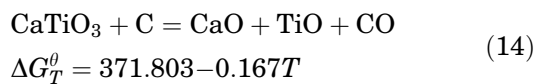
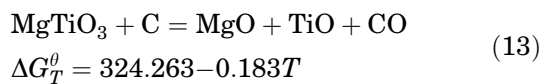
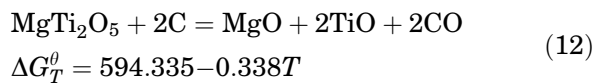
Next, the reduction reactions of the complicated titanium oxides were analyzed. Equations 12–15 demonstrate the reduction reactions of the titanium oxides by solid carbon, and the Gibbs free energy changes were calculated by the FactSage 7.0. The results are shown in Fig. 1. As calculated from Eqs. 12–15, the reduction temperatures of the complicated titanium oxides to TiO are 1485.4°C

Table I. Chemical composition of metallized pellet (wt.%)

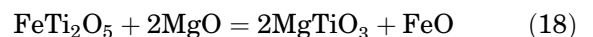
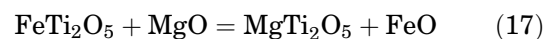
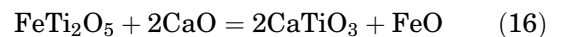
<u>TFe</u>	<u>MFe</u>	<u>TiO₂</u>	<u>V₂O₅</u>	<u>CaO</u>	<u>SiO₂</u>	<u>MgO</u>	<u>Al₂O₃</u>	<u>C</u>	<u>S</u>
71.38	64.56	15.53	0.82	1.01	3.71	2.58	3.83	0.036	0.027

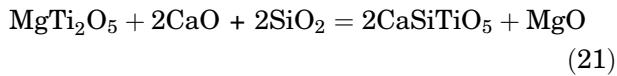
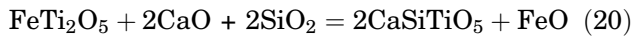
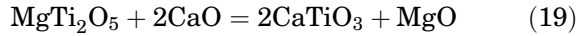

 Fig. 1. The $\Delta G-T$ curves of Eqs. 6–11 (a), Eqs. 12–15 (b) and Eqs. 16–21 (c).

(MgTi_2O_5), 1498°C (MgTiO_3), 1953.3°C (CaTiO_3), and 1663.3°C (CaSiTiO_5), respectively. The reduction temperatures of these titanium oxides are higher than the reduction temperatures of both the iron and vanadium oxides.



When the additives (CaO and MgO) were used for the adjustment of the slag compositions, the possible reactions involving CaO and MgO additions during smelting are expressed by Eqs. 16–21. The results are shown in Fig. 1. Apparently, the CaO addition during the electric furnace smelting process is beneficial to the CaTiO_3 and CaSiTiO_5 formation, whereas the MgO addition promotes the MgTi_2O_5 and MgTiO_3 formation. The formations of both CaTiO_3 and CaSiTiO_5 are easier than the MgTi_2O_5 and MgTiO_3 formation due to the corresponding lower changes of Gibbs free energy. Therefore, the effects of CaO and the MgO content in the slag on the reduction of iron, vanadium and titanium oxides are crucial in smelting.





It is inferred from the thermodynamic analysis that the increase of the smelting temperature and duration will promote the reductions. Moreover, more difficult reduction of titanates can be realized by CaO and MgO additions.

RESULTS AND DISCUSSION

Effects of Binary Basicity

In order to investigate the effects of the binary basicity on the reduction behaviors of the iron, vanadium and titanium oxides during smelting, a series of experiments were conducted at 1550°C for 20 min with the addition of 2% reductants. Figure 2a demonstrates that, as the binary basicity increases, the Fe recovery ratio increases, whereas the V recovery ratio increases as the binary basicity increases from 0.9 to 1.2. Beyond the binary basicity of 1.2, the V recovery ratio decreases. This observation can be explained by the decrease of slag viscosity as the basicity increased in a suitable range,²⁷ which promotes the vanadium diffusion. In addition, high melting point compounds are formed at a higher basicity, increasing the slag melting temperature, and deteriorating the vanadium reduction and diffusion conditions. Figure 2b demonstrates that, as the basicity increases from 0.9 to 1.2, the Ti content in the iron slag decreases, followed by a gradual increase of the Ti grade in the iron if the basicity is beyond 1.2. Apparently, the titanium oxides reduction is mitigated as the binary basicity increases in the range of 1.1–1.2. In addition, the TiO₂ activity in the titanium slag with various binary basicity values was calculated by the FactSage 7.0. As shown in Fig. 2c, the TiO₂ activity decreases as the basicity increases. Therefore, the titanium oxides reduction becomes more difficult with increasing the TiO₂ activity in the slag as the binary basicity increases. Therefore, the optimum binary basicity is 1.1.

Effects of MgO Content

The effects of MgO content in the slag on the reduction behaviors of the oxides were investigated under the conditions of binary basicity of 1.1, smelting temperature of 1550°C, the duration of 20 min and the reductant addition of 2%. Figure 3a demonstrates that the Fe recovery ratio increases slightly, whereas the V recovery ratio increases obviously as the MgO content in the slag increases. The increase of MgO content reduces the slag viscosity, consequently promoting the aggregation

and settlement of the molten iron. This is beneficial to the separation between the molten iron and the titanium slag.²⁸ As shown in Fig. 3b, when the MgO content is below 11%, increasing the MgO content has a weak effect on the Ti content in the molten iron, whereas the Ti content in the molten iron increases as the MgO increases further. This result indicates that the content of MgO in the slag should be controlled within a suitable range. In addition, FactSage 7.0 was utilized for the calculation of TiO₂ activity in the titanium slag and the results are presented in Fig. 3c. The TiO₂ activity decreases as the MgO content increases. Therefore, the reduction of titanium oxides is restrained by increasing the MgO content.

Effects of Smelting Temperature

The effects of the smelting temperature on the reduction behaviors of oxides of iron, vanadium and titanium were investigated in the temperature range of 1525–1600°C. Figure 4a shows that the smelting temperature has a dramatic effect on the recovery ratios of Fe and V during smelting. It can be observed that the Fe and V recovery ratios increase as the smelting temperature increases, whereas the recovery ratios decrease when the smelting temperature exceeds 1575°C. Figure 4b demonstrates that the Ti content in the molten iron increases rapidly as the smelting temperature increases. In addition, Figs. 2c and 3c show that the TiO₂ activity increases as the smelting temperature increases. To obtain higher Fe and V contents with a low Ti content in the molten iron, the optimum smelting temperature is 1550°C.

Effects of Smelting Duration

Several experiments were performed for exploration of the effects of smelting duration. Figure 5a demonstrates that the Fe and V recovery ratios increase as the smelting duration increases. In addition, as shown in Fig. 5b, the Ti content in the molten iron also increases as the smelting duration increases. Considering energy consumption during smelting, the smelting time duration should be controlled to 20 min.

Effects of Reductant Content

To investigate the effects of reductant content on the reduction behaviors of iron, vanadium and titanium oxides, several experiments were executed under the following smelting conditions: 1550°C, 20 min and binary basicity of 1.1. The results are shown in Fig. 6. When the reductant content increases from 2% to 5%, the Fe recovery ratio remains at 99.5% and the V recovery ratio increases from 79.61% to 95.52%. The Ti content in the molten iron also increases. Therefore, the optimum reductant content is 3%.

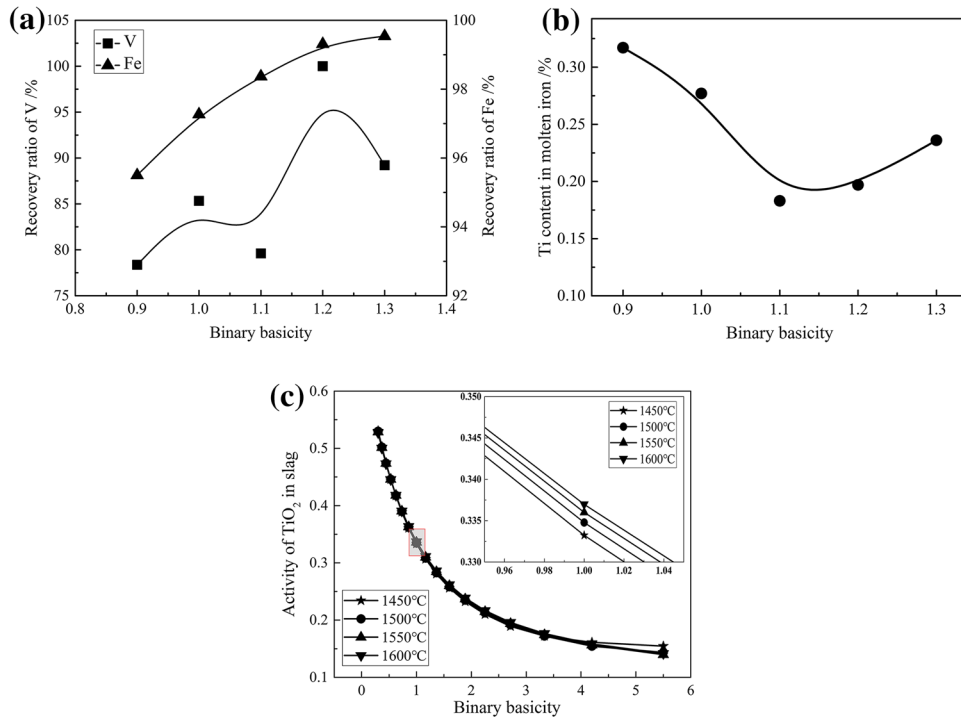


Fig. 2. Effects of binary basicity on the recovery ratios of Fe and V (a), Ti content in molten iron (b) and TiO_2 activity in slag (c).

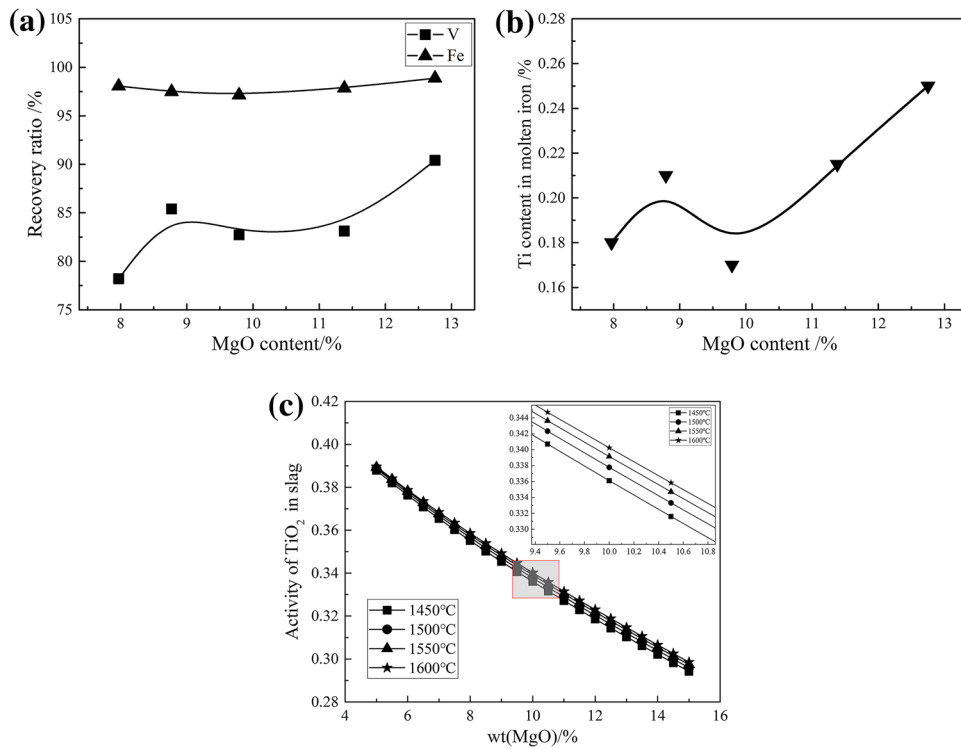


Fig. 3. Effects of MgO on the recovery ratios of Fe and V (a), Ti content in molten iron (b)²¹ and TiO_2 activity in slag (c).

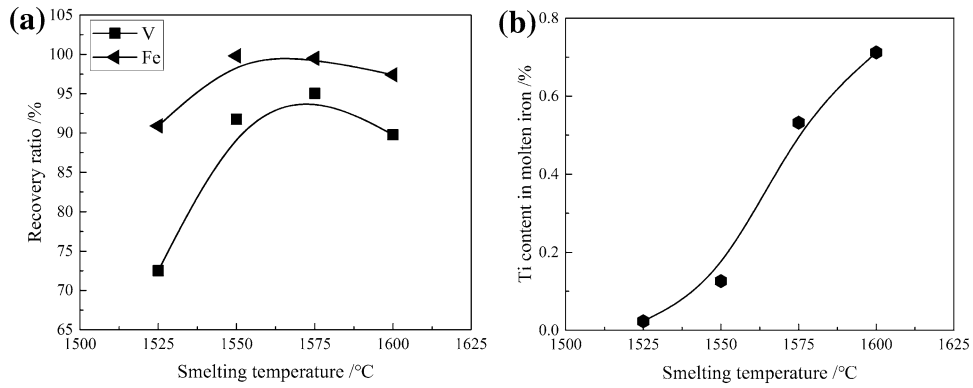


Fig. 4. Effects of smelting temperature on the recovery ratios of Fe and V (a), Ti content in molten iron (b).

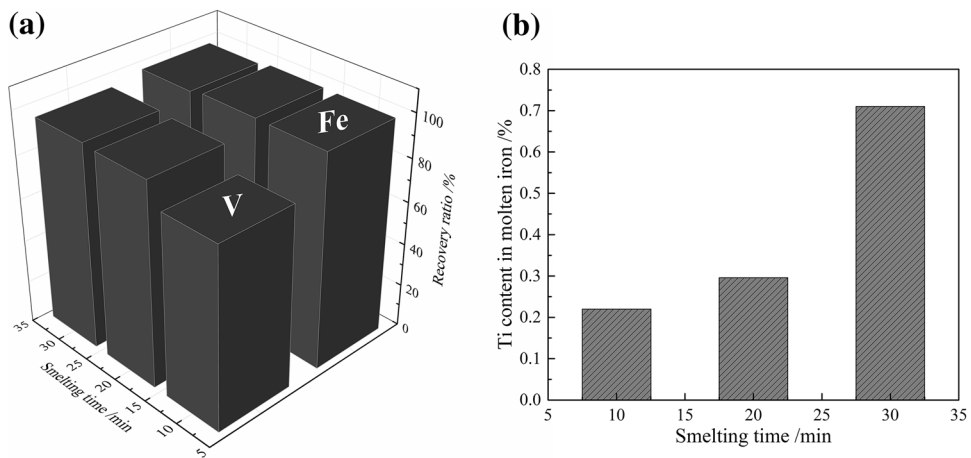


Fig. 5. Effects of smelting duration on the recovery ratios of Fe and V (a), Ti content in molten iron (b).

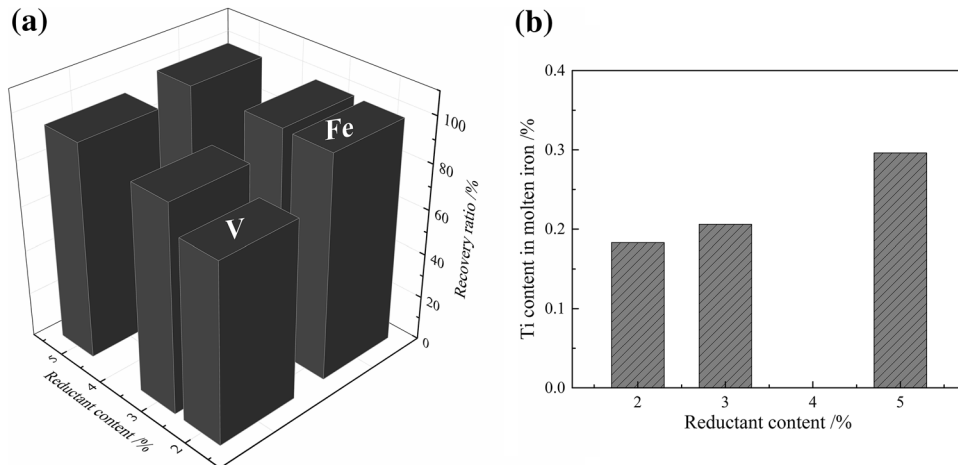


Fig. 6. Effects of reductant content on the recovery ratios of Fe and V (a), Ti content in molten iron (b).

CONCLUSION

The reduction behaviors of iron, vanadium and titanium oxides in the direct reduction–electric furnace smelting of vanadium titanomagnetite

metallized pellets were investigated in the present study. The results indicated that the reduction of iron and vanadium oxides is improved when the slag binary basicity increases from 0.9 to 1.2,

whereas the titanium oxides reduction is mitigated as the slag binary basicity increases. The MgO increment in the slag promotes the reduction of iron, vanadium and titanium oxides. The titanium oxides reduction is mitigated by increasing the basicity and MgO grade in the titanium slag. The Fe and V recovery ratios and the Ti content in the molten iron are increased as the smelting temperature, duration and reductant content increase. Furthermore, the TiO_2 activity is decreased as the titanium slag binary basicity and the MgO content in the slag increase.

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