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Influence of composition and temperature on distribution behavior of V, Ti and Si in HIsmelt

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Abstract: The effect of temperature and composition on the distribution behavior of V, Ti and Si in HIsmelt smelting vanadium−titanium magnetite was investigated, and the feasibility of HIsmelt smelting vanadium−titanium magnetite with natural basicity was evaluated. The thermodynamic calculations showed that higher FeO content and basicity, and lower C content and temperature are favorable for improving vanadium and titanium distribution ratio. However, reducing basicity and FeO content benefits the recovery of vanadium and titanium resources in hot metal and slag. It is proposed that in the HIsmelt smelting vanadium and titanium magnetite, the basicity is kept between 1.1 and 1.2, and the temperature is in the range of 1400−1450 °C. The experimental results indicate that there are difficulties in HIsmelt smelting vanadium−titanium magnetite with natural basicity.
Key words: vanadium−titanium magnetite; HIsmelt; distribution behavior; efficient recycling; viscosity

1 Introduction

The efficient recycling of V, Ti, Fe, and other metal resources lies at the heart of the comprehensive utilization of vanadium−titanium magnetite [1]. Currently, the blast furnace process is the primary vanadium−titanium magnetite melting process in China [2−4]. In the process of BF smelting vanadium−titanium magnetite, the TiO_2 content of the slag is typically between 22% and 25%, and it is difficult to recycle due to titanium element dispersion in the fine mineral phases [5,6]. Additionally, because ordinary iron ore is usually added to vanadium−titanium magnetite to decrease slag viscosity, the mass fraction of titanium and vanadium in slag and metal is decreased, and the strong reducing atmosphere in the blast furnace reduces the TiO_2 in the slag and generates TiC and TiN with a high melting point, which deteriorates the viscosity and lowers the TiO_2 content in the slag [7−9]. Therefore, it is difficult to recover Ti from blast furnace slag.

In contrast, HIsmelt smelting reduction is better suited to smelt vanadium−titanium magnetite. Iron ore powder, flux, and coal powder are used and directly sprayed into the metal bath to produce hot metal in the smelting reduction furnace (SRV) [10]. HIsmelt avoids the adverse influence of TiO_2 in vanadium−titanium magnetite on sintering processes and it has the advantage of energy conservation and environmental protection [11,12]. More importantly, HIsmelt has a weakly oxidizing slag composition and atmosphere, which inhibits the formation of TiC and TiN phases and increases the TiO_2 content of the slag [11,13,14]. As a result, HIsmelt slag has

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a viscosity tolerance of about twice that of blast furnace slag [15]. Furthermore, HIsmelt process has the advantages of high hot metal quality and low pollution emissions, making it one of the promising ironmaking processes [16−20]. Consequently, HIsmelt is suitable for smelting vanadium−titanium magnetite.

The stability of HIsmelt smelting vanadium−titanium magnetite strongly depends on the flow behavior of titanium-containing slag [5]. Previously, many scholars have studied the influence of temperature on the viscosity of titanium-containing slag system. MA et al [5,7] studied the change of slag viscosity with temperature under different TiO_2 conditions, the results showed that the slag viscosity reduced with rising temperature when the slag basicity was 1.2, and the temperature of critical viscosity of the slag grew with increasing TiO_2 content. Many studies [21−23] have been published on the distribution rules of vanadium and titanium in blast furnace smelting vanadium titanium-magnetite. JIAO et al [22] investigated the effect of chemical composition and smelting temperature on elemental partitioning in slag iron based on the production data from a blast furnace. Results showed that decreasing the operating temperature and the carbon content in the iron contributed to reducing the Ti distribution in the iron. ZHANG et al [21] studied the effects of temperature, slag composition, and slag-iron ratio on the distribution behavior of vanadium elements, the results showed that the vanadium distribution ratio in slag increased with the increase of smelting temperature and SiO_2 content.

However, the HIsmelt process differs from the blast furnace process in terms of raw material state, smelting atmosphere, and conditions. In addition, little has been published on the HIsmelt smelting vanadium−titanium magnetite, and even less on the vanadium and titanium distribution behavior of this process. It is necessary to investigate the distribution behavior and influencing factors of V and Ti in HIsmelt smelting vanadium−titanium magnetite. Therefore, in this work, the distribution behavior of V, Ti and Si in HIsmelt smelting vanadium−titanium magnetite was investigated using FactSage thermodynamic calculations, and proposed reasonable smelting process parameters in an actual production situation. Furthermore, through analyzing the results of thermodynamic calculations and experiments, the feasibility of HIsmelt smelting vanadium−titanium magnetite with natural basicity was discussed, which is beneficial to realizing a high proportion and simultaneous recovery of V and Ti resources in industrialized production.

2 Experimental

2.1 Thermodynamic calculations

The simplified chemical composition of vanadium−titanium magnetite from Panzhihua, China, was used in the calculation, and the phase composition is shown in Fig. 1. The basicity (CaO/SiO_2) was adjusted by varying the CaO addition to examine the effect of basicity on the elemental distribution ratio between slag and metal, and then the composition of the synthesized materials was normalized. In addition, FactSage was used to calculate the amount of graphite required for reduction and hot metal carburization to 4% based on the raw material composition, as shown in Table 1.

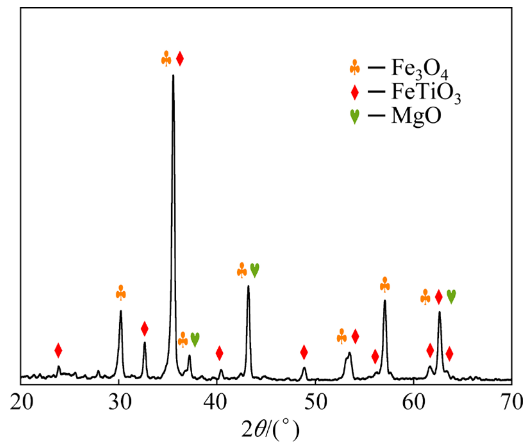

Fig. 1 XRD pattern of vanadium−titanium magnetite

The FactSage 8.1 thermodynamic package [24] was used for calculation in this study. It is assumed that all elements in the slag are present in the form of oxides [25]. The Equilib module was chosen to calculate the liquidus temperature of the slag and the composition of slag and metal for vanadium−titanium magnetite smelting by HIsmelt, with oxygen additions open in the calculations and the target window parameters for the composition in the dissolved phase were set. The viscosity module was selected to calculate the viscosity of the slag. Furthermore, the FactPS, Ftoxid, and Ftmisc databases were applied to the calculations.

Table 1 Chemical composition of materials (wt.%)

No.	Basicity	Total iron	CaO	SiO_2	Al_2O_3	MgO	V_2O_5	TiO_2	Graphite
1	0.3	57.30	0.91	3.05	2.89	2.90	0.64	11.12	5.85
2	0.6	56.77	1.81	3.02	2.87	2.88	0.63	11.01	5.79
3	0.9	56.26	2.69	2.99	2.84	2.85	0.62	10.92	5.74
4	1.2	55.76	3.56	2.97	2.82	2.83	0.62	10.82	5.69
5	1.5	55.27	4.41	2.94	2.79	2.80	0.61	10.72	5.64

In the first stage, the equilibrium composition of slag and metal was calculated separately, with basicity levels ranging from 0.3 (natural basicity) to 1.5, the C content of the metal ranging from 1% to 5%, and the FeO content of the slag ranging from 1% to 7%. Based on the composition of the slag and metal, the distribution ratios of V, Ti and Si were calculated.

Subsequently, the liquidus temperature and viscosity of slag were calculated according to the composition of slag and metal obtained from the thermodynamic calculations above. It should be noted that the calculations do not account for kinetics, and that in industrial production, the slag and metal do not reach chemical equilibrium due to smelting time constraints. Thus, the actual industrial slag and metal may differ from these calculations, but the trends are similar [26].

The elemental distribution was defined as follows [27]:

$$L_{\mathrm{M}}=\frac{w(\mathrm{MO}_x)}{w(\mathrm{M})} \tag{1}$$

where M is the V, Ti and Si elements, w(M) and $w(\mathrm{MO}_x)$ are the mass fraction of the M elements in metal and M oxides in slag individually, and L_{M} is the distribution ratio of M elements [25,27].

The binary basicity (R) is defined as follows, and w(CaO) and $w(SiO_2)$ are the mass fractions of CaO and SiO_2 in the slag.

$$R=\frac{w(\mathrm{CaO})}{w(\mathrm{SiO_2})} \tag{2}$$

2.2 Synthetic slag samples

The slag composition is based on the optimal slag composition obtained by thermodynamic calculation (R=0.3, w(FeO)=4%, w(MgO)=11.59%, $w(Al_2O_3)$=11.55%, $w(TiO_2)$=44.31%, and $w(V_2O_3)$=1.81%) to investigate the feasibility of HIsmelt smelting vanadium−titanium magnetite with natural basicity. The experimental reagents of CaO, SiO_2, Al_2O_3, MgO and TiO_2 were roasted at 900 °C in an argon atmosphere for 2 h, and $Fe_2C_2O_4$ was used to produce FeO at 1200 °C according to the reaction: $Fe_2C_2O_4$(s)=FeO(s)+CO(g)+CO_2(g). The carbonate and hydroxide in the reagents were decomposed during the heating, which reduced experimental error through the removal of CO_2 and H_2O. Afterward, 45 g of synthetic slag was thoroughly mixed and compacted under 20 MPa for the experiment. The purity of the reagents used and their suppliers are shown in Table 2.

Table 2 Purity of reagents and their suppliers

Material No.	Chemical	Purity/%	Supplier
1	CaO	98	Sinopharm Chemical Co., Ltd
2	SiO_2	99	Sinopharm Chemical Co., Ltd
3	Al_2O_3	99	Sinopharm Chemical Co., Ltd
4	MgO	98.5	Sinopharm Chemical Co., Ltd
5	TiO_2	98	Sinopharm Chemical Co., Ltd
6	V_2O_3	≥95	Strem Chemicals Co., Ltd
7	$Fe_2C_2O_4$	99	McLean Biochemical Co., Ltd.

2.3 Viscosity measurements

The slag viscosity was measured by the rotating cylinder method with the RTW-10 elevated temperature viscometer, and the schematic diagram is shown in Fig. 2. The slag vessel is a Mo crucible nested in a graphite crucible, and the pre-melting synthetic slag with basicity of 0.3 was placed in a constant temperature zone in a tube furnace. During the initial heating, high-purity Ar gas (99.99%) was

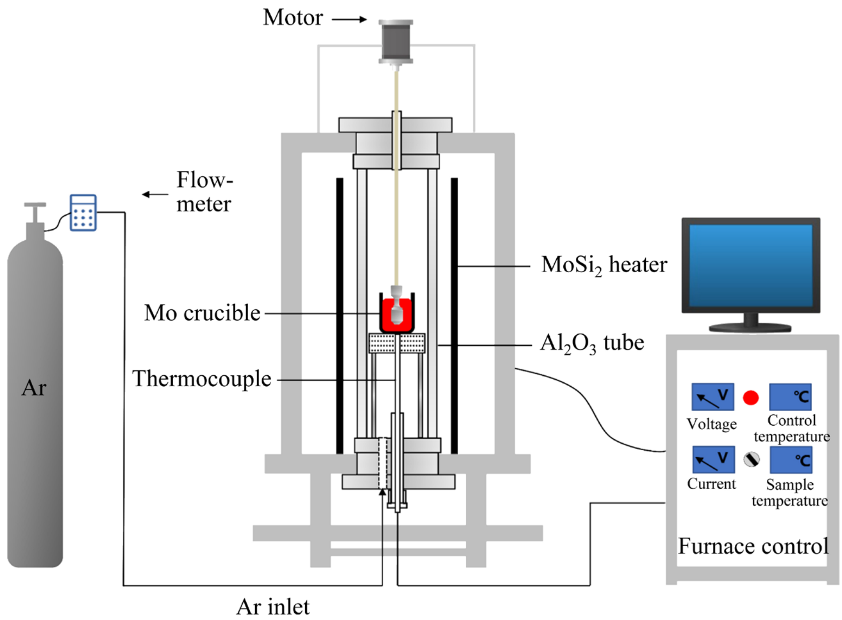

Fig. 2 Schematic diagram of RTW-10 elevated temperature viscometer

blown into the Al_2O_3 tube at a rate of 3 L/min to prevent the oxidation of FeO in the slag. The slag was then heated up to 1600 °C at a rate of 5 °C/min and held for 2 h to homogenize the slag composition. After this, the slag temperature was cooled down at a rate of 3 °C/min, and the temperature−viscosity curve was obtained by continuously measuring the slag viscosity at a speed of 200 r/min [5].

2.4 Quenching experiments and sample characterization

To obtain the structure and phase of the slag at high temperatures, after the viscosity measurement, the temperature was raised to 1500 °C and held for half an hour. The slag sample was quickly removed and quenched with water. The phase information of the quenching slag samples was obtained by X-ray diffraction (XRD, Empyrean, PANalytical).

3 Results and discussion

3.1 Effects of FeO and C contents on V, Ti and Si distribution behaviors

3.1.1 FeO content

The effects of FeO and C contents on the distribution behavior of V, Ti and Si were investigated during HIsmelt smelting, where the smelting temperature is 1450 °C and the basicities are 0.3 and 1.2, respectively. As shown in Table 3, as the FeO content increased from 1% to 7%, the contents of Si, V and Ti in the hot metal gradually decreased, and the V_2O_3 content in the slag rose, but the contents of SiO_2 and TiO_2 showed a reducing trend. It can be interpreted as an increment in FeO content, which raises the slag oxygen potential and causes the elements in hot metal to oxidize. It is worth noting that the effect of FeO on the V_2O_3 content is more significant compared to TiO_2 and SiO_2, according to the trend of the oxide content. Therefore, it is essential to control the oxygen potential and FeO content in the HIsmelt SRV furnace to ensure that as much vanadium as possible is distributed into the metal [28].

Figure 3 shows the effect of FeO content and basicity on the activity of V_2O_3, TiO_2, and SiO_2 in slag during HIsmelt smelting. As shown in Fig. 3(a), the activity of V_2O_3 in slag rises and then decreases with increasing FeO content, whereas the activity of TiO_2 and SiO_2 decreases. Since FeO is the basic oxide, improving the FeO content in slag may reduce the activity of acidic oxides in the slag, and the increase of V_2O_3 activity is caused by the rise in V_2O_3 content in the slag [29]. The activity trend of V_2O_3, TiO_2 and SiO_2 is consistent with previous studies [23,30].

Based on the calculating data in Table 3, the equilibrium distribution ratios of V, Ti and Si were calculated by Eq. (1). Figure 4 displays that L_V, L_{Ti}, and L_{Si} increase with increasing FeO content in

Table 3 Component of slag and metal with different FeO contents at basicity of 0.3 and 1.2 (wt.%)

R	Metal					Slag				
	Fe	C	Si	Ti	V	FeO	Al_2O_3	MgO	V_2O_3	TiO_2
0.30	97.85	1.40	0.15	0.0515	0.54	1.0	13.83	13.87	0.30	52.96
	98.63	0.90	0.06	0.0074	0.41	2.0	13.50	13.55	0.86	51.93
	99.01	0.67	0.03	0.0025	0.28	3.0	13.28	13.32	1.32	51.07
	99.25	0.53	0.02	0.0012	0.20	4.0	13.08	13.13	1.64	50.33
	99.41	0.43	0.01	0.0006	0.14	5.0	12.91	12.96	1.84	49.68
	99.52	0.36	0.01	0.0004	0.10	6.0	12.75	12.80	1.96	49.07
	99.60	0.31	0.01	0.0002	0.07	7.0	12.60	12.65	2.03	48.49
1.20	98.80	0.76	0.0142	0.0020	0.42	1.0	12.06	12.10	0.71	46.27
	99.33	0.44	0.0046	0.0003	0.23	2.0	11.85	11.89	1.36	45.47
	99.55	0.31	0.0022	0.0001	0.13	3.0	11.69	11.73	1.67	44.85
	99.67	0.24	0.0013	0.0001	0.09	4.0	11.55	11.59	1.81	44.31
	99.74	0.19	0.0008	0.0000	0.06	5.0	11.42	11.46	1.88	43.81
	99.78	0.16	0.0005	0.0000	0.04	6.0	11.29	11.33	1.91	43.32
	99.82	0.14	0.0004	0.0000	0.03	7.0	11.17	11.21	1.92	42.85

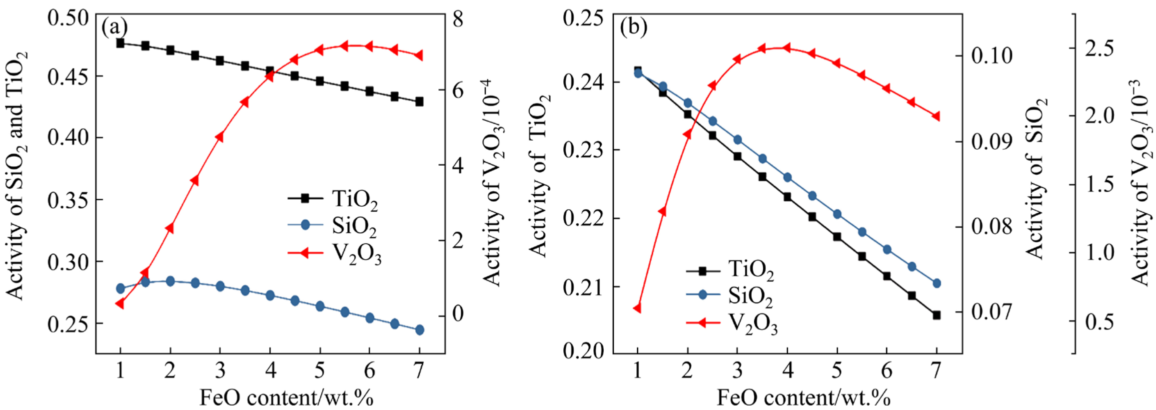

Fig. 3 Effects of basicity of 0.3 (a) and 1.2 (b) on V_2O_3, TiO_2 and SiO_2 activities in slag at 1450 °C

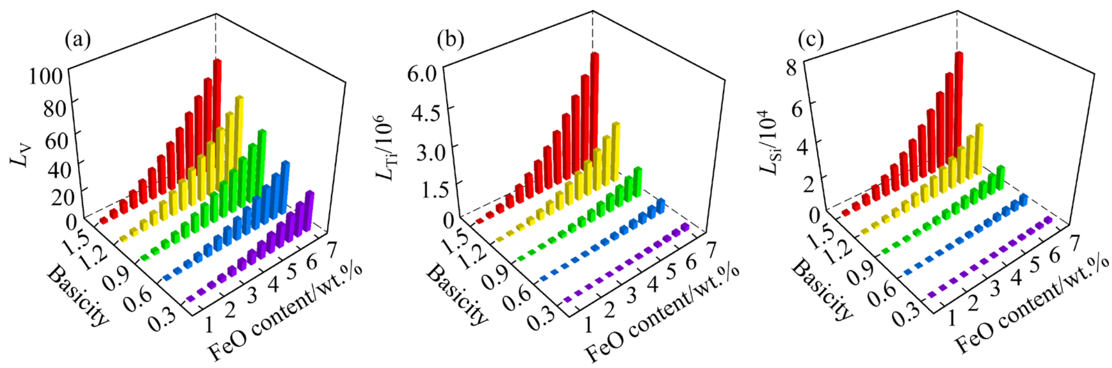

Fig. 4 Distribution of V (a), Ti (b) and Si (c) with FeO content in slag at 1450 °C

HIsmelt slag. This is due to the decrease of TiO_2 and SiO_2 activity in the slag, and the reduction of titanium and silicon oxides could be suppressed.

Figure 5 reveals that the viscosity and melting temperature of slag decrease with increasing FeO content in slag at different basicity levels during

HIsmelt smelting, which is consistent with the results of LI et al [31,32]. It can be speculated that FeO has basic oxide properties, which will diminish the polymerization of the Si—O and Al—O tetrahedral structures and decompose their network structure at high temperatures [29,33]. Thermodynamic calculations show that higher FeO content improves the fluidity of the slag and raises the Ti and Si distribution, but it will oxidize vanadium into the slag and reduce the TiO_2 content in the slag, which is detrimental to the extraction of vanadium from the hot metal and the utilization of TiO_2 resources, the FeO content of the slag should therefore be kept low.

Previous studies [28,34] have revealed that higher FeO content and oxygen partial pressure reduce the vanadium content in the hot metal. Additionally, under the experimental conditions [30], the V content was below 0.13% when the FeO content in the slag was higher than 4.5%. Consequently, the FeO content of the slag should be less than 4.5% when smelting vanadium− titanium magnetite in HIsmelt.

3.1.2 C content

As shown in Table 4, as the C content in the hot metal increases from 1% to 5%, a significant amount of V_2O_3 and TiO_2 is reduced into the hot metal. This indicates that decreasing the carburization is favorable to the recovery of titanium resources in the slag, but not to the vanadium extraction in the hot metal during HIsmelt smelting vanadium−titanium magnetite.

Figure 6 illustrates that reducing C content will ascend the V and Ti distribution during HIsmelt smelting vanadium−titanium magnetite, which is generally consistent with previous studies [22]. It

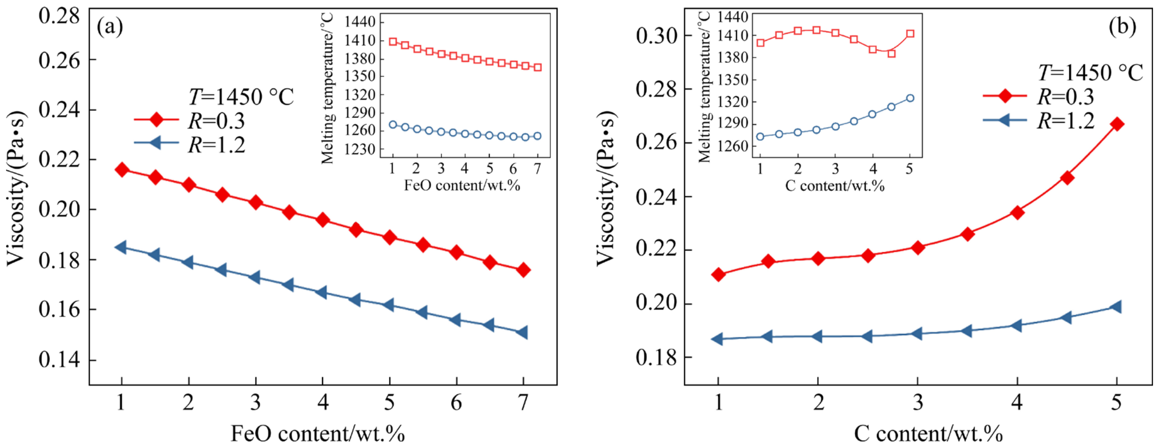

Fig. 5 Changes in slag viscosity and melting temperature with FeO (a) and C (b) content

Table 4 Slag and metal components at different basicities with different C contents (wt.%)

R	Metal					Slag				
	Fe	C	Si	Ti	V	FeO	Al_2O_3	MgO	V_2O_3	TiO_2
0.30	98.47	1.00	0.07	0.01	0.45	1.71	13.58	13.63	0.69	52.21
	96.81	2.00	0.29	0.32	0.58	0.56	14.21	14.26	0.10	53.17
	94.28	3.00	0.30	1.83	0.58	0.39	15.45	15.51	0.03	49.55
	91.09	4.00	0.16	4.18	0.57	0.38	17.69	17.75	0.02	41.21
	87.78	5.00	0.06	6.61	0.55	0.33	21.20	21.27	0.01	28.76
1.20	98.47	1.00	0.03	0.01	0.50	0.68	12.15	12.19	0.41	46.58
	97.13	2.00	0.11	0.17	0.59	0.23	12.39	12.43	0.05	46.82
	95.01	3.00	0.15	1.26	0.59	0.13	13.04	13.09	0.01	44.36
	92.10	4.00	0.08	3.24	0.57	0.11	14.36	14.41	0.01	38.42
	89.06	5.00	0.04	5.35	0.55	0.09	16.23	16.29	0.00	30.09

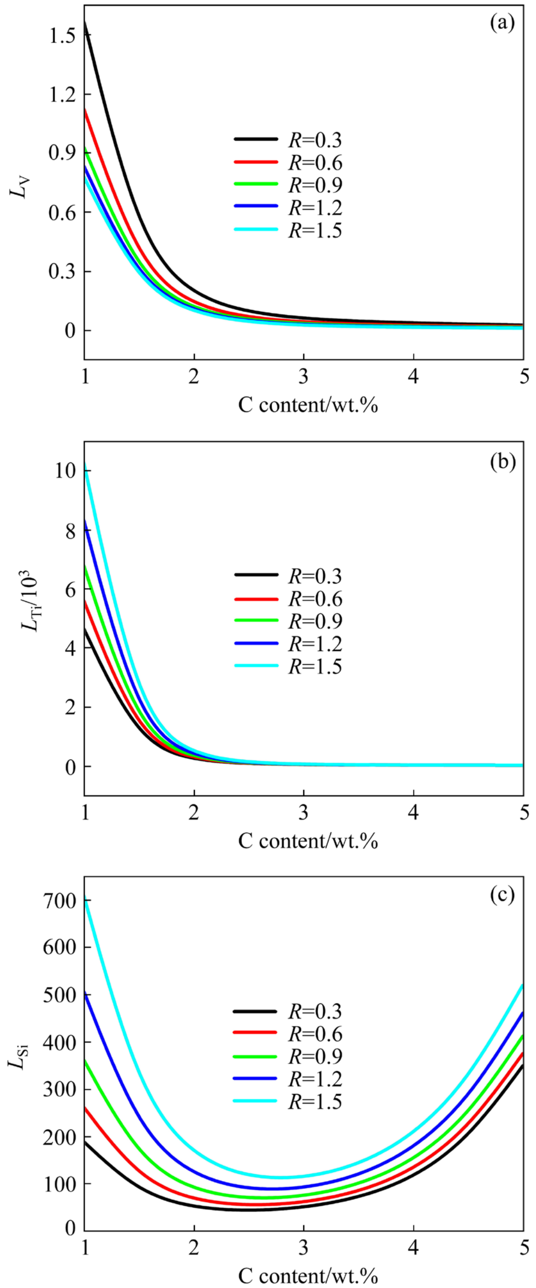

Fig. 6 Changes of V (a), Ti (b) and Si (c) distribution with C content in hot metal at 1450 °C

should be noted that as the C content increases, the Si distribution decreases and then increases, implying that a reasonable C content keeps the Si content at a low level in the hot metal. In addition, dissolved carbon in hot metal influences slag flow characteristics indirectly by acting on slag composition. Figure 5 displays that the slag viscosity and melting temperature rise as the C content increases. The carburization of the hot metal promotes an excessive reduction reaction of TiO_2 in the slag, forming TiC and TiN with high melting points, thus deteriorating the slag fluidity.

In the process of HIsmelt smelting ordinary iron ore, the C content in the hot metal is generally maintained at around 4.2%, the ore fines and coal powders react with the liquid slag and metal in a solid−liquid equation and melt immediately after spraying into the molten pool. If the C content of the hot metal is excessively low, the iron, vanadium, and other elemental oxides in the mineral powder cannot be rapidly reduced into the hot metal, so raising C content is conducive to improved production efficiency. However, a higher C content is not advantageous to the efficient utilization of titanium resources and the control of the silicon content in the hot metal. Based on thermodynamic calculations, it is proposed that the carbon content of the hot metal should be in the range of 3.5%−4.5% in industrial production.

3.2 Effect of basicity on distribution behaviors of V, Ti and Si

It is evident from Table 5 that as the basicity decreases, the content of V in hot metal and TiO_2 in slag grows, helping in the efficient recycling and comprehensive utilization of vanadium and titanium resources. As shown in Fig. 4, the slag basicity has a positive effect on the distribution of V, Ti and Si at 1450 °C. Furthermore, the Si content strongly correlates with the Ti content in hot metal at 1450 °C, and the distribution rates of Si and Ti are essentially consistent, which can be explained as Si can reduce titanium oxides according to Eq. (3) [35]. Thus, both the Si and Ti contents of hot metal should be controlled at a low level to inhibit the formation of TiC and TiN.

$$TiO_2+[Si]=[Ti]+SiO_2,\quad \Delta G^{\Theta}_{1723K}=-11958.63\ \text{J/mol [36]} \tag{3}$$

FactSage was used to calculate the slag viscosity and liquidus temperature at various basicities based on the data in Tables 4 and 5. Figure 7 shows that the viscosity of slag diminishes with the increasing basicity, which may be explained by the fact that CaO is a basic oxide and the rise of free Ca^{+2} in the slag with the rising basicity, which breaks the covalent bonds of SiO_2 and Al_2O_3 and thus leads to a decrease in viscosity [22,25]. Nevertheless, the liquidus temperature of slag drops and then grows as the basicity increases, and the slag with the basicity of 1.2 has the minimum liquidus temperature. Figure 8

Table 5 Composition of slag and metal with 4% C and 4% FeO at 1450 °C (wt.%)

No.	*R*	Metal					Slag				
		Fe	C	Si	Ti	V	FeO	Al_2O_3	MgO	V_2O_3	TiO_2
1	0.30	91.09	4.00	0.16	4.18	0.57	0.38	17.69	17.75	0.019	41.21
2	0.60	91.46	4.00	0.13	3.85	0.57	0.23	16.42	16.48	0.012	40.20
3	0.90	91.79	4.00	0.10	3.54	0.56	0.15	15.30	15.35	0.009	39.33
4	1.20	92.10	4.00	0.08	3.24	0.57	0.11	14.36	14.41	0.008	38.42
5	1.50	92.39	4.00	0.07	2.97	0.57	0.08	13.52	13.57	0.006	37.61
6	0.30	99.25	0.53	0.0198	0.0012	0.20	4.00	13.08	13.13	1.64	50.33
7	0.60	99.46	0.38	0.0071	0.0004	0.15	4.00	12.54	12.58	1.74	48.09
8	0.90	99.59	0.29	0.0029	0.0001	0.11	4.00	12.01	12.05	1.78	46.17
9	1.20	99.67	0.24	0.0013	0.0001	0.09	4.00	11.55	11.59	1.81	44.31
10	1.50	99.73	0.20	0.0006	0.0000	0.07	4.00	11.11	11.15	1.79	42.69

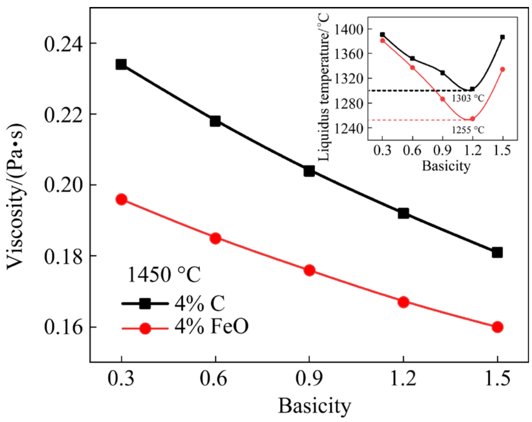

Fig. 7 Changes in slag viscosity and liquidus temperature with basicity (The calculated data are based on Tables 4 and 5)

shows the liquid phase projection of slag with different basicities, the results reveal that the liquid phase region expands with elevating basicity.

According to data from the HIsmelt plant in China, the slag basicity is typically in the range of 1.1−1.2, and the slag properties are excellent. Thermodynamic calculations show that as slag basicity increases, utilizing vanadium and titanium resources becomes more difficult. However, the slag fluidity improves, and the liquidus temperature drops and reaches the lowest level at a basicity of 1.2. Since excessive slag viscosity can result in liquid flooding, it is advised that the slag basicity is between 1.1 and 1.2 for the HIsmelt smelting of vanadium−titanium magnetite. In addition, the preferred slag and metal compositions in thermodynamic calculations are compositions No. 4 and No. 9 in Table 5.

3.3 Effect of temperature on V, Ti and Si distribution behaviors

Previous research [37] has shown that temperature has a negative effect on the vanadium distribution. As shown in Fig. 9, the L_V, L_{Ti}, and L_{Si} decrease with increasing temperature at different basicity levels. The rising temperature promotes the reduction reaction of vanadium, titanium, and silicon oxides, as well as the V distribution into the hot metal, but reduces the TiO_2 content of the slag.

Figure 8 shows that the liquid phase region of slags at different basicities expands with increasing temperature. Figure 10 depicts the relationship between the slag viscosity and temperature. It demonstrates that the slag viscosity diminishes with rising temperature and stabilizes in the temperature range of 1400−1450 °C. To sum up, it is proposed that the melting temperature of the HIsmelt SRV furnace is kept between 1400 and 1450 °C in industrial production.

3.4 Feasibility of smelting vanadium−titanium magnetite with natural basicity

The feasibility of smelting natural basicity vanadium−titanium magnetite by HIsmelt is discussed. Thermodynamic calculations show that for the vanadium−titanium magnetite with natural basicity, the TiO_2 content in slag and V content in hot metal are significantly high, which facilitates the efficient recycling of titanium and vanadium resources. However, Figs. 7 and 10 depict that the natural basicity melting slag has a high viscosity and melting temperature.

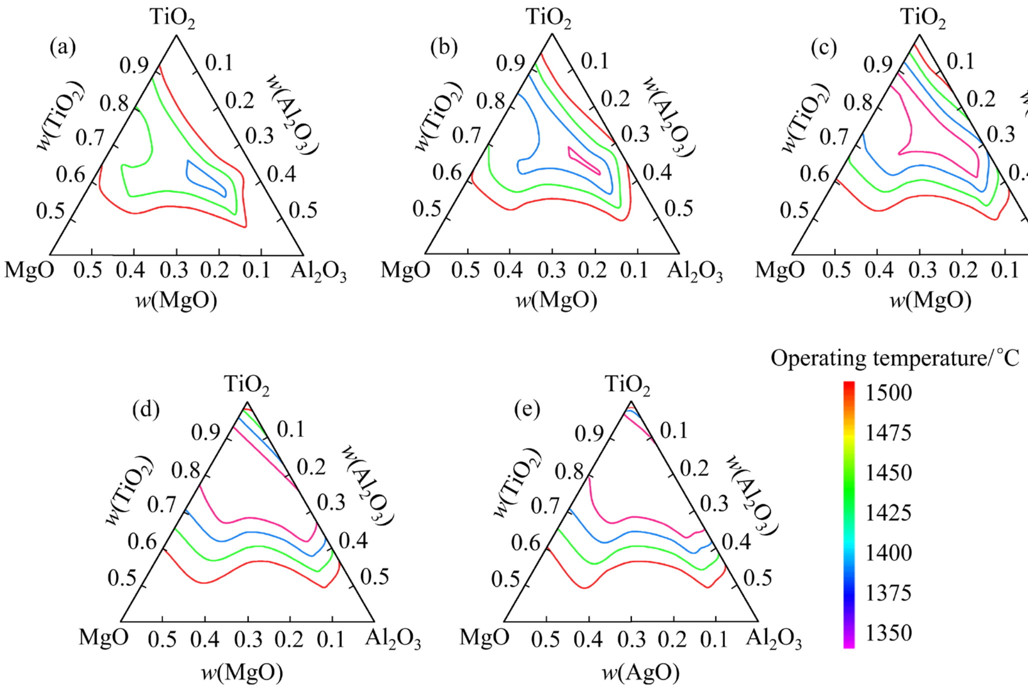

Fig. 8 Liquid phase projection of slag with different basicities (TiO_2−Al_2O_3−MgO−CaO−SiO_2−FeO, 4% FeO): (a) R=0.3; (b) R=0.6; (c) R=0.9; (d) R=1.2; (e) R=1.5

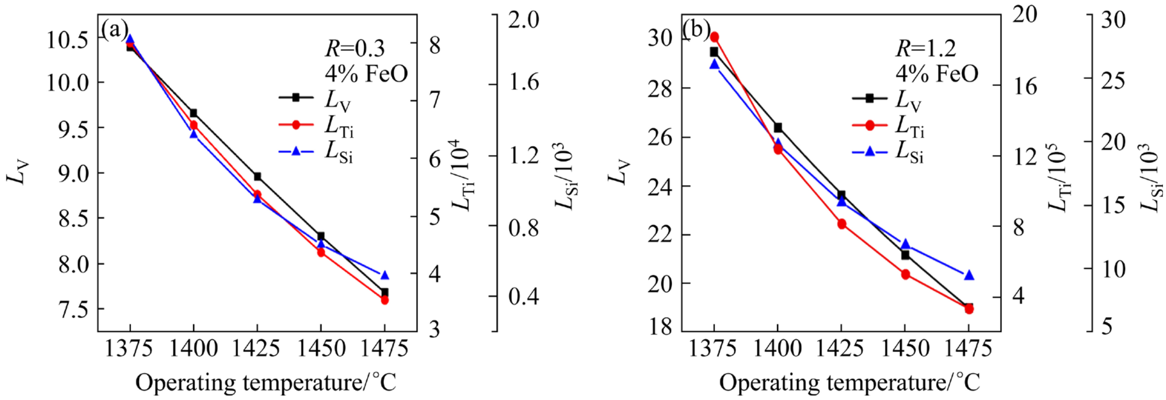

Fig. 9 Changes in distribution of V, Ti and Si with temperature

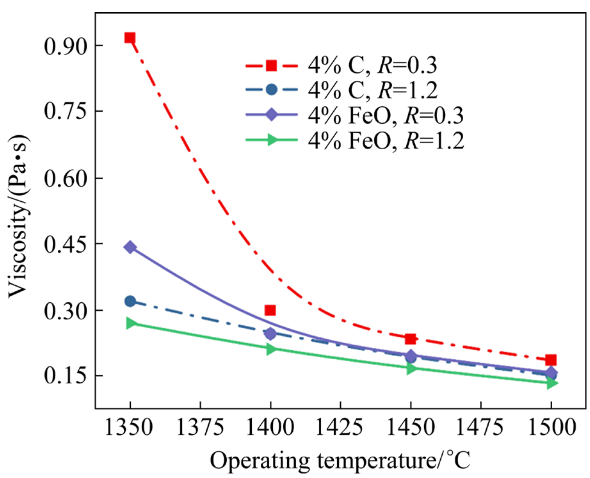

Fig. 10 Changes in slag viscosity with temperature

The viscosity experiment shows that the viscosity of the natural basicity slag increases as the temperature reduces, with a steep rise and a significant inflection point when the temperature is decreased to 1572−1578 °C (Fig. 11). Since the smelting temperature for HIsmelt is generally less than 1500 °C [16], the natural basicity vanadium−titanium magnetite is not suitable for HIsmelt smelting. Furthermore, the experimental results demonstrated that FactSage could calculate the viscosity trend of high TiO_2 slag [38].

Figure 12 shows the XRD pattern of the natural basicity melting slag, and the main phase of natural basicity slag at 1500 °C is pseudobrookite.

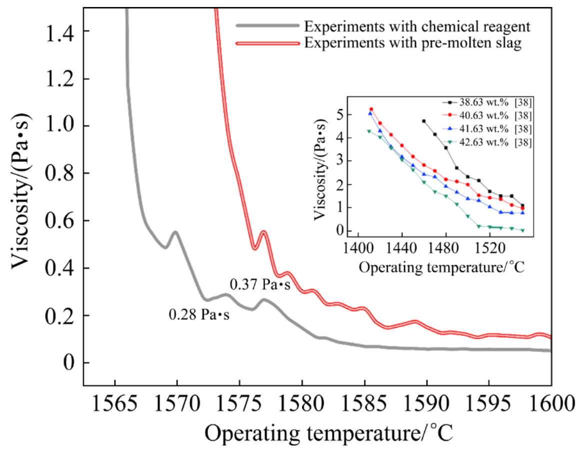

Fig. 11 Influence of temperature on viscosity of natural basicity slag

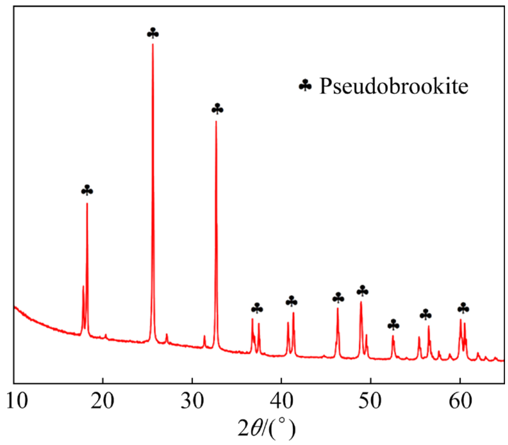

Fig. 12 XRD pattern of natural basicity melting slag

Some studies [39,40] have shown that without flux, the pseudobrookite phase with a high melting temperature was precipitated during ilmenite smelting, and pseudobrookite formation was more prominent at 1500 °C with a high content of TiO_2 in the system, which is consistent with the experimental results. In conclusion, the HIsmelt process is not currently suitable for smelting vanadium−titanium magnetite with natural basicity, and further research should be conducted to improve slag fluidity by optimizing the composition of low basicity slag.

4 Conclusions

(1) High FeO content and basicity, and low C content of hot metal and temperature are favorable to improve the V and Ti distribution. However, reducing basicity and FeO content benefit the recovery of vanadium and titanium resources in hot metal and slag.

(2) It is proposed that in the industrial production of HIsmelt smelting vanadium and titanium magnetite, the content of C in metal should be in the range of 3.5%−4.5%, FeO content of the slag should be less than 4.5%, the basicity is kept between 1.1 and 1.2, and the temperature is in the range of 1400−1450 °C.

(3) Decreasing the slag basicity can effectively improve the TiO_2 content of slag, but increases slag viscosity significantly. There are difficulties in HIsmelt smelting vanadium−titanium magnetite with natural basicity, further research should be conducted to improve slag fluidity by optimizing the slag composition.

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References

[1] XU Cheng-bao, ZHANG Yi-min, LIU Tao, HUANG Jiang. Characterization and pre-concentration of low-grade vanadium−titanium magnetite ore [J]. Minerals, 2017, 7(8): 137−148.

[2] ZHOU Mi, JIANG Tao, YANG Song-tao, XUE Xiang-xin. Vanadium–titanium magnetite ore blend optimization for sinter strength based on iron ore basic sintering characteristics [J]. International Journal of Mineral Processing, 2015, 142: 125−133.

[3] ZHOU Mi, JIANG Tao, DING Xue-yong, MA Shi-hong, WEI Guo, XUE Xiang-xin. Thermodynamic study of direct reduction of high-chromium vanadium−titanium magnetite (HCVTM) based on phase equilibrium calculation model [J]. Journal of Thermal Analysis and Calorimetry, 2019, 136(2): 885−892.

[4] TANG Wei-dong, XUE Xiang-xin, YANG Song-tao, ZHANG Li-heng, HUANG Zhuang. Influence of basicity and temperature on bonding phase strength, microstructure, and mineralogy of high-chromium vanadium−titanium magnetite [J]. International Journal of Minerals, Metallurgy, and Materials, 2018, 25(8): 871−880.

[5] MA Heng-bao, JIAO Ke-xin, ZHANG Jian-liang, ZONG Yan-bing, ZHANG Jian, MENG Sai. Viscosity of $CaO-MgO-Al_2O_3-SiO_2-TiO_2-FeO$ slag with varying TiO_2 content: the effect of crystallization on viscosity abrupt behavior [J]. Ceramics International, 2021, 47(12): 17445−17454.

[6] ZHANG L, ZHANG L N, WANG M Y, LI G Q, SUI Z T. Recovery of titanium compounds from molten Ti-bearing

blast furnace slag under the dynamic oxidation condition [J]. Minerals Engineering, 2007, 20(7): 684−693.

[7] MA Heng-bao, JIAO Ke-xin, ZHANG Jian-liang. The influence of basicity and TiO_2 on the crystallization behavior of high Ti-bearing slags [J]. CrystEngComm, 2020, 22(2): 361−370.

[8] ZHANG Shu-shi, HU Peng, RAO Jia-ting, WANG Zhen-yang, ZHANG Jian-liang, ZONG Yan-bing. Comprehensive utilization status of vanadium−titanium magnetite and feasibility analysis of HIsmelt smelting [J]. Journal of Central South University (Science and Technology), 2021, 52(9): 3085−3092. (Chinese)

[9] KURUNOV I F. The direct production of iron and alternatives to the blast furnace in iron metallurgy for the 21st century [J]. Metallurgist, 2010, 54(5): 335−342.

[10] STEPHENS D, TABIB M, SCHWARZ M P, DAVIS M. CFD simulation of bath dynamics in the HIsmelt smelt reduction vessel for iron production [J]. Progress in Computational Fluid Dynamics, 2012, 12(2/3): 196−206.

[11] LI You-ling, LI Hui-bin, WANG Hua, QING Shan, HU Jian-hang, HOU Ya-li, LI Hu, LI Liang-qing. Smelting potential of HIsmelt technology for high-phosphorus iron ore and ilmenite [C]//2011 International Conference on Computer Distributed Control and Intelligent Environmental Monitoring. Changsha, China: IEEE, 2011: 1283−1286.

[12] CAO Chao-zhen, MENG Yu-jie, YAN Fang-xing, ZHANG Dian-wei, LI Xin, ZHANG Fu-ming. Analysis on energy efficiency and optimization of HIsmelt process [M]. Cham: Springer International Publishing, 2019: 3−11.

[13] LI Lin. Basic research on Hismelt ironmaking process [D]. Beijing: University of Science and Technology Beijing, 2020. (in Chinese)

[14] SCHENK J L. Recent status of fluidized bed technologies for producing iron input materials for steelmaking [J]. Particuology, 2011, 9(1): 14−23.

[15] JACQUES P. HIsmelt technology suitable for vanadium-titanium magnetite [C]//2010 Annual Conference of Non-blast furnace Ironmaking and Seminar on Comprehensive Utilization of Vanadium−titanium Magnetite. Panzhihua, China: CSM, 2010: 233−238. (in Chinese)

[16] ZHANG Jian-liang, ZHANG Guan-qi, LIU Zheng-jian, WANG Zhen-hua, LI Ke-jiang, ZHANG Xie-bing. Production overview and main characteristics of HIsmelt process in Shandong Molong [J]. China Metallurgy, 2018, 28(5): 37−41. (in Chinese)

[17] JIA Li-jun. Iron bath molten pool smelting technology-HIsmelt smelting reduction smelting technology [C]//2018 Nickel laterite industry conference and APOL annual conference. Chengdu, China: APOL, 2018: 51−54. (in Chinese)

[18] LIU Wei-zao, TENG Liu-mei, ROHANI S, QING Zhi-feng, ZHAO Bin. CO_2 mineral carbonation using industrial solid wastes: A review of recent developments [J]. Chemical Engineering Journal, 2021, 416: 129093.

[19] HE Min-yu, TENG Liu-mei, GAO Xu-xiang, ROHANI S, REN Shan. Simultaneous CO_2 mineral sequestration and rutile beneficiation by using titanium-bearing blast furnace slag: Process description and optimization [J]. Energy, 2022. 248: 123643.

[20] REN Shan, ALDAHRI T, LIU Wei-zao, LIANG Bin. CO_2 mineral sequestration by using blast furnace slag: From batch to continuous experiments [J]. Energy, 2021, 214: 118975.

[21] ZHANG Y L, ZHAO F, WANG Y G. Effects of influencing factors on distribution behaviors of vanadium between hot metal and $FeO-SiO_2-MnO(-TiO_2)$ slag system [J]. Steel Research International, 2011, 82(8): 940−950.

[22] JIAO Ke-xin, CHEN Chun-lin, ZHANG Jian-liang, LIU Zheng-jian, WANG Guang-wei, WANG Wen-peng, SHAO Qiu-jun. Analysis of titanium distribution behaviour in vanadium-containing titanomagnetite smelting blast furnace [J]. Canadian Metallurgical Quarterly, 2018, 57(3): 274−282.

[23] WANG Shu-ai, GUO Yu-feng, JIANG Tao, CHEN Feng, ZHANG Fu-qiang, YANG Ling-zhi. Behavior of silicon during reduction and smelting of vanadium titanomagnetite metallized pellets in an electric furnace [J]. JOM, 2019, 71(1): 329−335.

[24] BALE C W, BÉLISLE E, CHARTRAND P, DECTEROV S A, EIRKSSON G. Reprint of Factsage thermochemical software and databases, 2010−2016 [J]. Calphad, 2016, 55: 1−19.

[25] HUANG Q Y, LV X W, HUANG R, SONG J J. Preparation of Ti−Si−Al alloy by aluminothermic reduction of TiO_2 bearing blast furnace slag [J]. Canadian Metallurgical Quarterly, 2013, 52(4): 413−421.

[26] SCHELLER P R, LACHMANN S, KLINKENBERG C, HULKA K, WEISS A. Nb-alloyed Cr-steel in simulated strip casting process [J]. ISIJ International, 2006, 46(12): 1865−1870.

[27] WANG Zhen-yang, ZHANG Jian-liang, XING Xiang-dong, LIU Zheng-jian. Congregated electron phase and Wagner model applied in titanium distribution behavior in low-titanium slag [J]. Transactions of Nonferrous Metals Society of China, 2015, 25(5): 1640−1647.

[28] DIAO Jiang, ZHANG Quan, LIU Xuan, CHEN Lian, XIE Bing. Indirect determination of equilibrium distribution of V and Cr between liquid slag and solid iron at 1653 K and 101.3 kPa [J]. Metallurgical Research & Technology, 2016, 114(1): 112.

[29] MA Shu-fang, LI Ke-jiang, ZHANG Jian-liang, JIANG Chun-he, SUN Min-min. Structural characteristics of $CaO-SiO_2-Al_2O_3-FeO$ slag with various FeO contents based on molecular dynamics simulations [J]. JOM, 2021, 73: 1637−1645.

[30] HOWARD R L, RICHARDS S R, WELCH B J, MOORE J J. Vanadium distribution in melts intermediate to ferroalloy production from vanadiferous slag [J]. Metallurgical and Materials Transactions B, 1994, 25(1): 27−32.

[31] LI Yun, LI Yong-quan, FRUEHAN R J. Formation of titanium carbonitride from hot metal [J]. ISIJ International, 2001, 41(12): 1417−1422.

[32] LI Yun, FRUEHAN R J. Thermodynamics of TiCN and TiC in $Fe-C_{sat}$ melts [J]. Metallurgical and Materials Transactions B, 2001, 32(6): 1203−1205.

[33] WU Ting, WANG Qian, YU Cheng-feng, HE Sheng-ping. Structural and viscosity properties of $CaO-SiO_2-Al_2O_3-FeO$ slags based on molecular dynamic simulation [J]. Journal of Non-Crystalline Solids, 2016, 450: 23−31.

[34] LI Y Z. Thermodynamic analysis of vanadium blowing process in bottom blowing oxygen converter [J]. Journal of College of Maanshan Iron and Steel, 1984, (01): 12−22. (in Chinese)

[35] PANG Zheng-de, LV Xue-wei, JIANG Yu-yang, LING Jia-wei, YAN Zhi-min. Blast furnace ironmaking process with super-high TiO_2 in the slag: Viscosity and melting properties of the slag [J]. Metallurgical and Materials Transactions B, 2020, 51(2): 722−731.

[36] HUANG X H. Principles of iron and steel metallurgy [M]. 4th ed. Beijing: Metallurgical Industry Press, 2013. (in Chinese)

[37] ZHEN Xiao-peng, XIE Bing, ZHAO Chong-yang, HUANG Qing-yun. Vanadium distribution behavior at the endpoint of vanadium extraction by converter process [J]. Journal of University of Science and Technology Beijing, 2012, 34(12): 1371−1378. (in Chinese)

[38] MA Jing, FU Gui-qin, LI Wei, ZHU Miao-yong. Influence of TiO_2 on the melting property and viscosity of Cr-containing high-Ti melting slag [J]. International Journal of Minerals, Metallurgy and Materials, 2020, 27(3): 310−318.

[39] GUPTA A K, AULA M, PIHLASALO J, MÄKELA P, HUTTULA M, FABRITIUS T. Preparation of synthetic titania slag relevant to the industrial smelting process using an induction furnace: 3 [J]. Applied Sciences, 2021, 11(3): 1153.

[40] KIM D H, HEO J H, PARK H S, KIM J K, PARK J H. Improving the production efficiency of high-titania slag in ti extraction process: Fluxing effect on formation of pseudobrookite [J]. Scientific Reports, 2020, 10(1): 6530.

成分和温度对 HIsmelt 中钒、钛和硅分配行为的影响

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摘 要：研究 HIsmelt 冶炼钒钛磁铁矿过程中温度和成分对钒、钛和硅分配行为的影响，并探讨 HIsmelt 冶炼自然碱度钒钛磁铁矿的可行性。热力学计算表明，更高的炉渣 FeO 含量、碱度，更低的温度和铁水含 C 量有利于提高钒和钛元素的分配比。然而，降低炉渣碱度和 FeO 含量有利于渣铁中钛和钒资源的回收。建议在 HIsmelt 冶炼钒钛磁铁矿时，碱度保持在 1.1～1.2 范围内，温度在 1400～1450 ℃范围内。结果表明，HIsmelt 工艺冶炼自然碱度钒钛磁铁矿存在困难。

关键词：钒钛磁铁矿；HIsmelt；分配行为；高效回收；黏度

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