



# Recovery of Fe, V, and Ti in modified Ti-bearing blast furnace slag

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**Abstract:** A two-stage oxidation—alkali leaching—acid leaching method was proposed to recovery Fe, V, and Ti in modified Ti-bearing blast furnace slag. The optimal experiment conditions of iron extraction were one-stage oxidation time 40 s and holding time 8 min. The recovery rate of iron was 89.93%. The optimum experiment conditions of vanadium extraction were total oxidation time of 126 s, NaOH concentration of 4.0 mol/L, leaching temperature of 95 °C, leaching time of 90 min, and the number of cycle was 4. The leaching rate of vanadium was 92.13%. The optimal experiment conditions of titanium extraction were HCl concentration of 4.5 mol/L, leaching temperature of 75 °C, and leaching time of 90 min. The TiO<sub>2</sub> content of synthetic rutile was 98.61%.

**Key words:** Ti-bearing blast furnace slag; oxidation; modification; leaching; synthetic rutile; pig iron

## 1 Introduction

China is rich in titanium resources, 95% of which are stored in the form of vanadium–titanium magnetite in the southwestern part of the country [1–3]. Currently, ore containing about 30% Fe, 10% TiO<sub>2</sub>, and 0.3% V<sub>2</sub>O<sub>5</sub> is smelted in blast furnaces at the Panzhihua Iron and Steel Corporation. Most Ti components in the ore are separated from iron and are enriched in the molten slag (22%–25% TiO<sub>2</sub>). More than 3 million tons of blast furnace slag are generated yearly in China. In the last few years, several methods for treating the slag have been studied, such as flotation separation, magnetic separation, hydrometallurgy and pyrometallurgy [4]. Nevertheless, the recovery efficiency of Ti components of those methods is relatively low, and the slag has not been used efficiently [5]. Owing to the dispersive distribution of Ti constituents in various fine-grained (<10 μm) mineral phases with complex interfacial combinations, it is difficult to recover them via

traditional separation methods.

Therefore, a method for the selective crystallization and separation of perovskite phase was proposed [6]. There are many studies [7–13] on enriching the titanium components in blast furnace slag into perovskite. Nevertheless, it has been proved that perovskite is different to be extracted due to its dendrite structure and the similar density with other phases. Compared to perovskite (density: 4.0 g/cm<sup>3</sup>), rutile possesses a high added value and high density (4.2–4.3 g/cm<sup>3</sup>). Therefore, it is appropriate to enrich Ti components to rutile phase. There is some research on the selective precipitation and separation of rutile phase. LI et al [14] investigated the crystallization behavior of rutile phase in modified titanium-bearing blast furnace slag. SUN et al [15] investigated the effect of P<sub>2</sub>O<sub>5</sub> and basicity on the crystallization behaviors of rutile phase in modified titanium-bearing blast furnace slag using the single hot thermocouple technique. ZHANG et al [16] studied the crystallization and coarsening kinetics of rutile in modified titanium-bearing blast furnace slag.

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ZHANG et al [17] proved the feasibility of alkali leaching—acid leaching of modified titanium-bearing blast furnace slag by potential–pH diagrams for extracting rutile. It is worth noting that most of the existing researches have focused on the crystallization and extraction of rutile phase in modified titanium-bearing blast furnace, but little for the extraction of metallic iron. ZHANG et al [18] studied the procedure to extract titanium components and metallic iron from modified titanium-bearing blast furnace slag. WANG et al [19] investigated the separation of iron droplets from modified titanium-bearing blast furnace slag. In the above two studies, all  $O_2$  was blown into the molten slag at one time to oxidize high melting point substances ( $TiC$  and  $TiN$ ), thereby reducing the viscosity of the molten slag and realizing the settlement of metallic iron. The  $TiO_2$  contents of the modified titanium-bearing blast furnace slag of the above two studies are less than 30%. There are no reports about the research of extraction of metallic iron from modified titanium-bearing blast furnace slag with a high  $TiO_2$  content (47%).

This study aimed to explore the recovery of Fe, V, and Ti in modified Ti-bearing blast furnace slag by two-stage oxidation—alkali leaching—acid leaching. The oxidation, alkali leaching, and acid leaching conditions were optimized by single-factor experiments. Moreover, the mechanisms of

extraction of metallic iron and vanadium were discussed.

## 2 Experimental

### 2.1 Materials

In this study, Ti-bearing blast furnace slag was purchased from Panzhihua Iron and Steel Research Institute (Sichuan province, China). Based on previous research [20], titanium slag was prepared from titanium middling ore. The additive,  $SiO_2$ , was of analytical grade and provided by China National Medicines Corporation Ltd. The  $O_2$  with a purity of 99% (mass fraction) was provided by Shenyang Shuntai Gas Corporation Ltd. The chemical compositions and XRD patterns of Ti-bearing blast furnace slag and titanium slag are shown in Table 1 and Fig. 1, respectively. It can be seen that Ti-bearing blast furnace slag mainly contains perovskite ( $CaTiO_3$ ), akermanite ( $Ca_2MgSi_2O_7$ ), diopside ( $CaMgSi_2O_6$ ), and spinel ( $MgAl_2O_4$ ). Anosovite and anorthite ( $CaAl_2(SiO_4)_2$ ) are the main phases in titanium slag.

### 2.2 Procedures

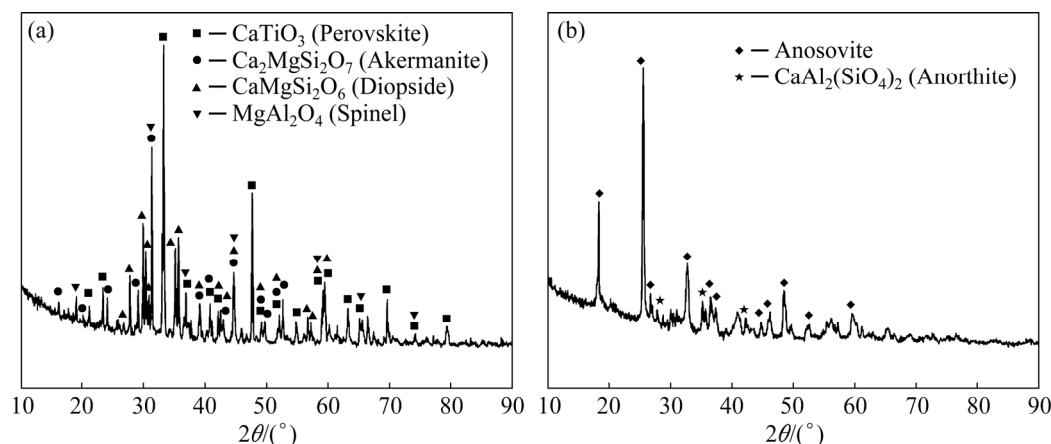
#### 2.2.1 Extraction of metallic iron

To study the mechanism of extraction of metallic iron, the standard Gibbs free-energy changes of relevant reactions were calculated by

**Table 1** Chemical components of samples (wt.%)

Sample No.	CaO	$SiO_2$	$TiO_2$	$Ti_2O_3$	$Al_2O_3$	MgO	FeO	MFe	$V_2O_5$	TiC+TiN
1	26.87	25.13	17.58	3.86	14.08	7.86	1.51	2.18	0.21	0.57
2	4.32	8.85	60.72	14.65	2.64	2.02	—	0.96	3.05	0.32

1: Ti-bearing blast furnace slag; 2: Titanium slag; MFe represents metallic iron content



**Fig. 1** XRD patterns of raw materials: (a) Ti-bearing blast furnace slag; (b) Titanium slag

FactSage. Further, the effect of oxidation time on the crystallization behavior of titanium-bearing mixed molten slag (titanium-bearing blast furnace slag and titanium slag) was simulated by FactSage. The Scheil-Gulliver cooling method in the Equilib module of FactSage was used to build the relationship between oxidation time and crystallized phases. To verify the authenticity of simulation results, the molten slags with one-stage oxidation time of 0, 42, 84, and 126 s were quenched in water.

The modification experiments were performed in a vertical  $\text{MoSi}_2$  furnace with a B-type thermocouple. It was estimated that the overall temperature accuracy of the experiment was  $\pm 3^\circ\text{C}$ . The oxidation gas was  $\text{O}_2$ , and the flow rate of  $\text{O}_2$  was 5 L/min. The  $\text{O}_2$  was blown into molten slag twice. According to the previous research [21,22], the added mass of titanium-bearing blast furnace slag, the added mass of titanium slag, the added mass of  $\text{SiO}_2$  and the total oxidation time were 222 g, 278 g, 40 g, and 126 s, respectively. The above raw materials were loaded into a crucible at  $1450^\circ\text{C}$  for 20 min to melt fully, and then  $\text{O}_2$  was blown into molten slag with a certain time (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 s). The oxidized molten slag was kept at  $1450^\circ\text{C}$  for a specified time (2, 4, 6, 8, 10 and 12 min), and then the remaining  $\text{O}_2$  was blown into molten slag. Subsequently, molten slag was slowly cooled to

room temperature at a cooling rate of  $5^\circ\text{C}/\text{min}$ . The cooled slag was called modified titanium-bearing blast furnace slag (MTBBFS). The mass of pig iron was weighed, and the content of metallic iron in the MTBBFS was analyzed. The purpose of modification experiments was to transform the titanium-bearing phases (perovskite and anosovite) in the raw materials (titanium-bearing blast furnace slag and titanium slag) into rutile phase. The rutile was the raw material of titanium white with the chloride process. The schematic diagram of the experimental process is shown in Fig. 2.

### 2.2.2 Extraction of vanadium

The modified experiments were carried out under the optimum conditions of iron extraction experiments, i.e., the  $\text{O}_2$  was blown into molten slag with an oxidation time of 40 s, and then the oxidized molten slag was held at  $1450^\circ\text{C}$  for 8 min. Subsequently, the remaining  $\text{O}_2$  (44, 65, 86, 107, 128, and 149 s) was blown into molten slag and the slag was slowly cooled to room temperature at a cooling rate of  $5^\circ\text{C}/\text{min}$ . Before alkali leaching, the modified slag was first ground to a particle size of less than  $150\ \mu\text{m}$ .

The experiments of alkali leaching were performed at atmospheric pressure in a 500 mL three-necked flask equipped with a reflux condenser. The reaction mixture was heated by a thermostatic water bath and agitated by a magnetic stirrer at a

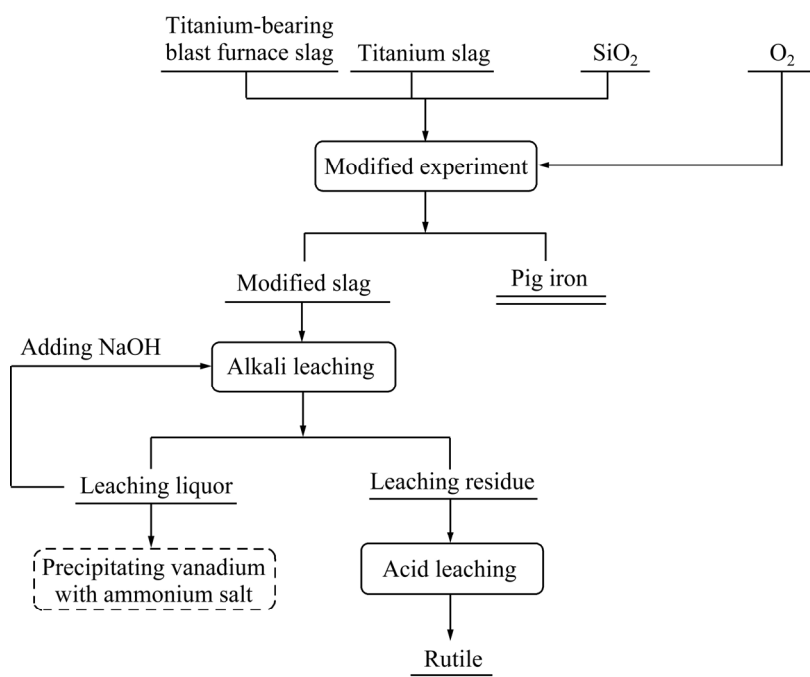


Fig. 2 Schematic diagram of experimental process

stirring rate of 500 r/min. For each experiment, the added mass of the MTBBFS was 100 g, and the liquid–solid ratio was fixed at 3 (mL/g).

According to a L/S of 3 (mL/g), the volume of alkali-leaching solution was 300 mL. Then, a concentration of NaOH solution (1.0–4.0 mol/L) was taken and poured into a three-necked flask. Once the specified temperature (25–95 °C) was reached, the MTBBFS was added to the reactor and leached for a certain time (30–180 min). Afterwards, the slurry was filtered to separate leaching residue from leaching liquor. The leaching residue was washed repeatedly with the distilled water until the washing fluid was neutral. The leaching liquor was first submitted for chemical analysis, and then was recycled by adding 30 g NaOH for the next alkali leaching. The leaching rate ( $\eta$ ) of V was calculated with Eq. (1):

$$\eta = \frac{m_L}{m_0} \times 100\% \quad (1)$$

where  $m_L$  is the mass of element in leaching liquor, and  $m_0$  is the mass of element in the MTBBFS.

### 2.2.3 Extraction of titanium

Before acid (HCl) leaching, the MTBBFS was first leached under the above optimal alkali (NaOH) leaching conditions. Then, the product of alkali leaching was leached by hydrochloric acid. The leaching residue was washed with distilled water, dried in an oven at 110 °C for 24 h, and submitted for chemical analysis. The experimental conditions of acid leaching: HCl concentration 2.0–5.0 mol/L, leaching temperature 25–85 °C, leaching time 30–180 min, a liquid–solid ratio of 3 (mL/g), and 100 g of alkali-leaching product.

## 2.3 Characterization

The chemical compositions of relevant samples were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, PerkinElmer Optima 4300DV). The ammonium ferric sulfate titration method [23] was used to determine the content of  $\text{TiO}_2$ . The potassium dichromate titration method [24] was used to determine the content of  $\text{Ti}_2\text{O}_3$ . According to the relevant references [25,26], the total content of TiC and TiN in the raw materials was determined. The phase compositions of relevant samples were identified by XRD analysis (X'PERT PROMPD/

PW3040, PANalytical B.V. Corp., The Netherlands) using Cu  $K_\alpha$  radiation for 7 min from 10° to 90°. The microscopic observation and element distribution of relevant samples were conducted by using a scanning electron microscopy (TESCAN VEGA III) equipped with an EDS spectrometer (INCA Energy 350). The viscosity of molten slag was measured through the rotating spindle method by the ZCN-1600 melt physical property comprehensive testing instrument with a digital viscometer. Quenched samples were observed by a metallographic microscope (201A-D). The standard Gibbs free energy changes of relevant reactions were calculated by the reaction module of FactSage software (version 7.1). The Equilib module of FactSage was used to build the relationship between oxidation time and the mass of crystallized phases. The Pourbaix diagrams of V–Ti–H<sub>2</sub>O systems at 25 and 100 °C were drawn by the  $E$ –pH module of FactSage. The databases of FactSage used in the above thermodynamic calculation were FToxid and FactPS.

## 3 Results and discussion

### 3.1 Extraction of metallic iron

#### 3.1.1 Extraction mechanism of metallic iron

To study the mechanism of extraction of metallic iron, the standard Gibbs free-energy changes of relevant reactions were calculated, and the results are shown in Fig. 3. It is well known that the reason for the high melting points of titanium-bearing blast furnace slag and titanium slag is that they contain high melting point substances, such as TiC and TiN. As shown in Fig. 3, the standard

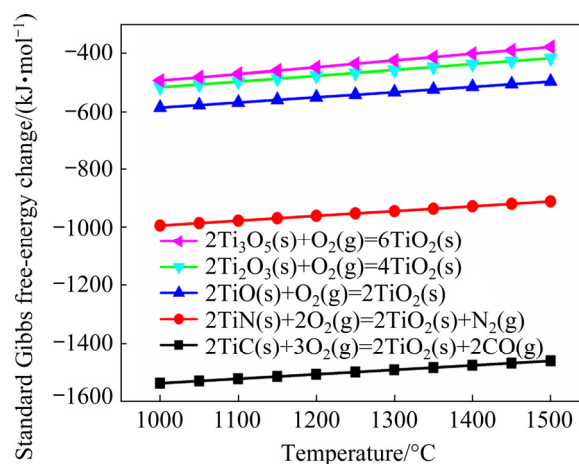


Fig. 3 Standard Gibbs free-energy changes of relevant reactions

Gibbs free-energy changes of the oxidation reactions of TiC and TiN are less than those of TiO, Ti<sub>2</sub>O<sub>3</sub>, and Ti<sub>3</sub>O<sub>5</sub>, implying that TiC and TiN are preferentially oxidized to TiO<sub>2</sub> when O<sub>2</sub> is blown into molten slag. The disappearance of TiC and TiN will result in a decrease in the viscosity of molten slag. While a decrease in the viscosity of molten slag is beneficial to the settling of metallic iron particles.

When all O<sub>2</sub> (total oxidation time 126 s) was blown into molten slag for one time, the SEM image and XRD pattern of the MTBBFS are shown in Fig. 4. It can be seen that the metallic iron was not settled. According to the previous research [21], when the content of TiO<sub>2</sub> in the raw materials was

29.17 wt.% and all O<sub>2</sub> was passed into molten slag for one time, metallic iron particles were settled to the bottom of the slag. We guessed that the TiO<sub>2</sub> content of the raw materials in this study increasing to 47 wt.% causes a large amount of rutile crystals to crystallize at 1450 °C, which increases the viscosity of molten slag and metallic iron particles could not be settled. Therefore, we would verify this conjecture through both theory and experiments.

The Scheil–Gulliver cooling method in the Equilib module of FactSage was used to build the relationship between oxidation time and the mass of crystallized phases, and the results are shown in Figs. 5 and 6. The relationship between the

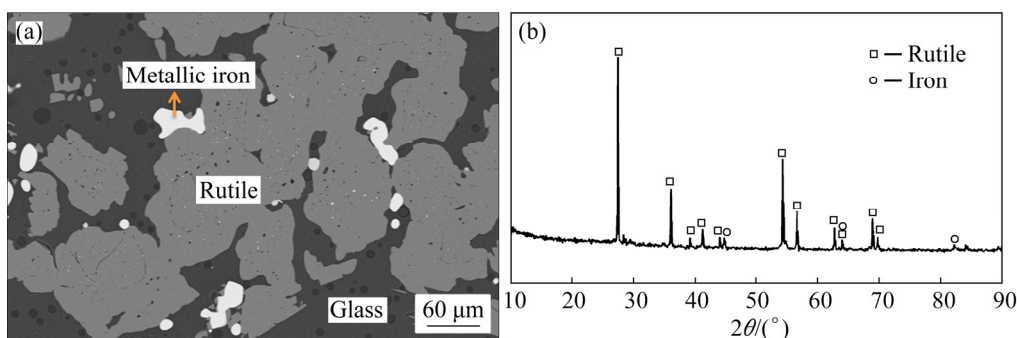


Fig. 4 SEM image (a) and XRD pattern (b) of MTBBFS

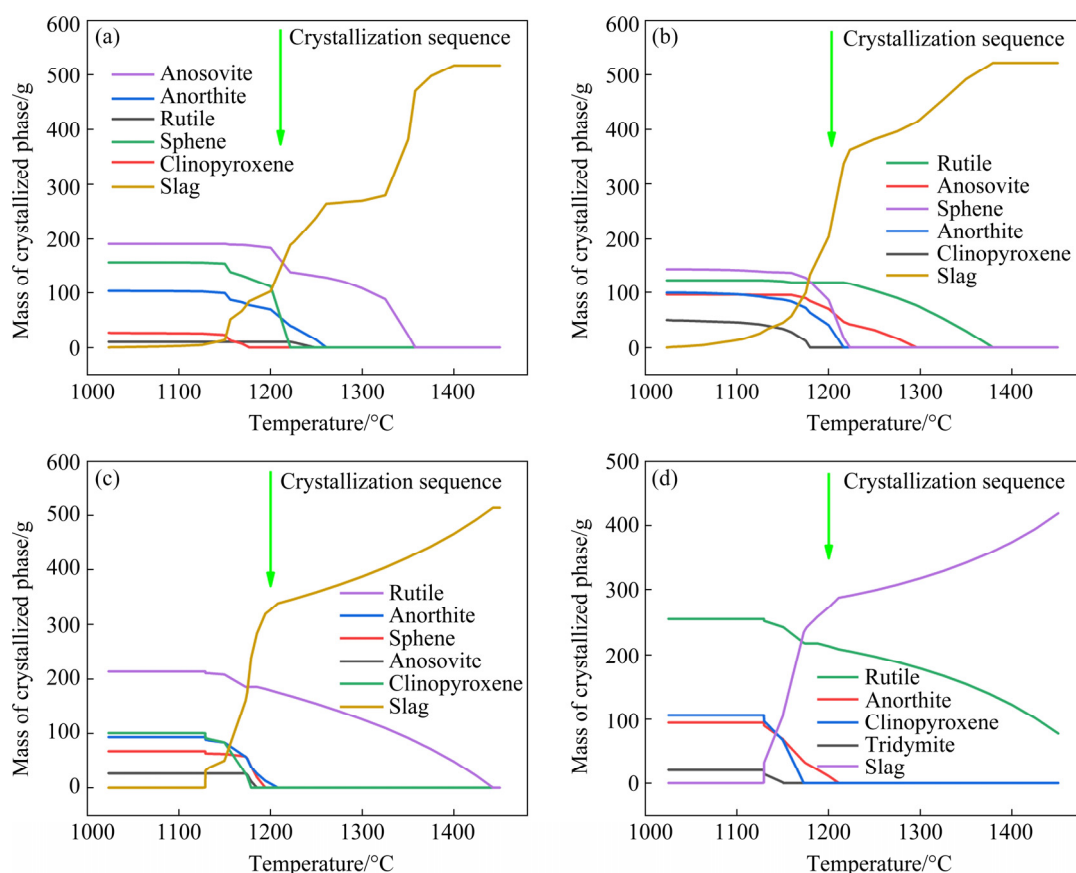
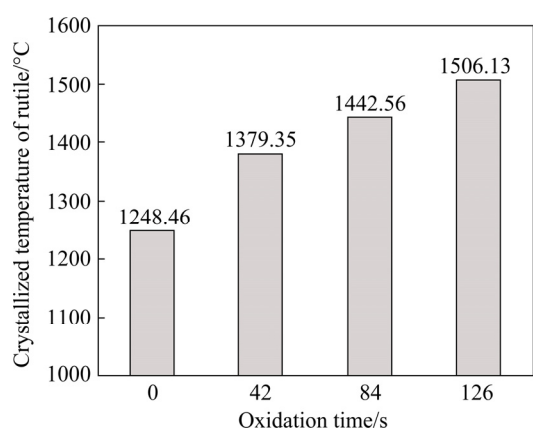
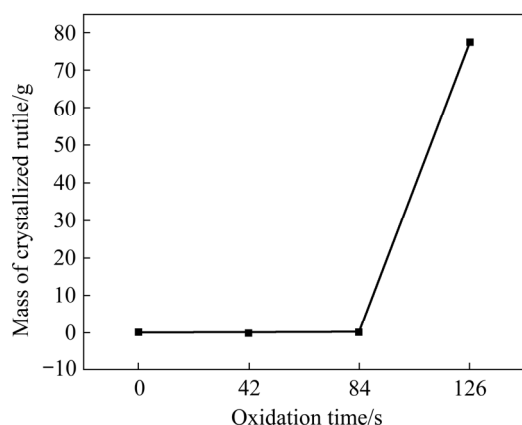


Fig. 5 Relationship between oxidation time and mass of crystallized phases: (a) 0 s; (b) 42 s; (c) 84 s; (d) 126 s



**Fig. 6** Relationship between crystallized temperature of rutile and oxidation time

crystallized temperature of rutile and oxidation time is illustrated in Fig. 6, and the relationship between the mass of crystallized rutile at 1450 °C and oxidation time is shown in Fig. 7. As shown in Figs. 5 and 6, when oxidation time was 0 s, the crystallized order of mineral phases in the MTBBFS was anosovite → anorthite → rutile → sphene → clinopyroxene. The first crystallized phase was anosovite and the crystallized temperature was 1357.62 °C. When oxidation time was 42 s, the crystallized order of phases in the MTBBFS was rutile → anosovite → sphene → anorthite → clinopyroxene. The first crystallized phase was rutile and the crystallized temperature was 1379.35 °C. When oxidation time was 84 s, the crystallized order of phases in the MTBBFS was rutile → anorthite → sphene → anosovite → clinopyroxene. The first crystallized phase was rutile and the crystallized temperature was 1442.56 °C. When oxidation time was 126 s, the crystallized order of phases in the MTBBFS was



**Fig. 7** Relationship between mass of crystallized rutile at 1450 °C and oxidation time

rutile → anorthite → clinopyroxene → tridymite. The first crystallized phase was rutile and the crystallized temperature was 1506.13 °C. As shown in Figs. 6 and 7, rutile crystals precipitated at 1450 °C when the oxidation time was 126 s. In summary, the crystallized temperature of rutile was greater than 1450 °C when the oxidation time was 126 s, implying that rutile crystallized at 1450 °C.

As shown in Fig. 8, when oxidation time was 0, 42, and 84 s, no rutile crystals were found in the quenched samples. When oxidation time increased to 126 s, rutile crystals were observed in the quenched sample. The above results indicate that rutile crystals crystallized when oxidation time was 126 s. The crystallization of rutile crystals led to an increase in the viscosity of molten slag, which inhibited the settling of metallic iron particles.

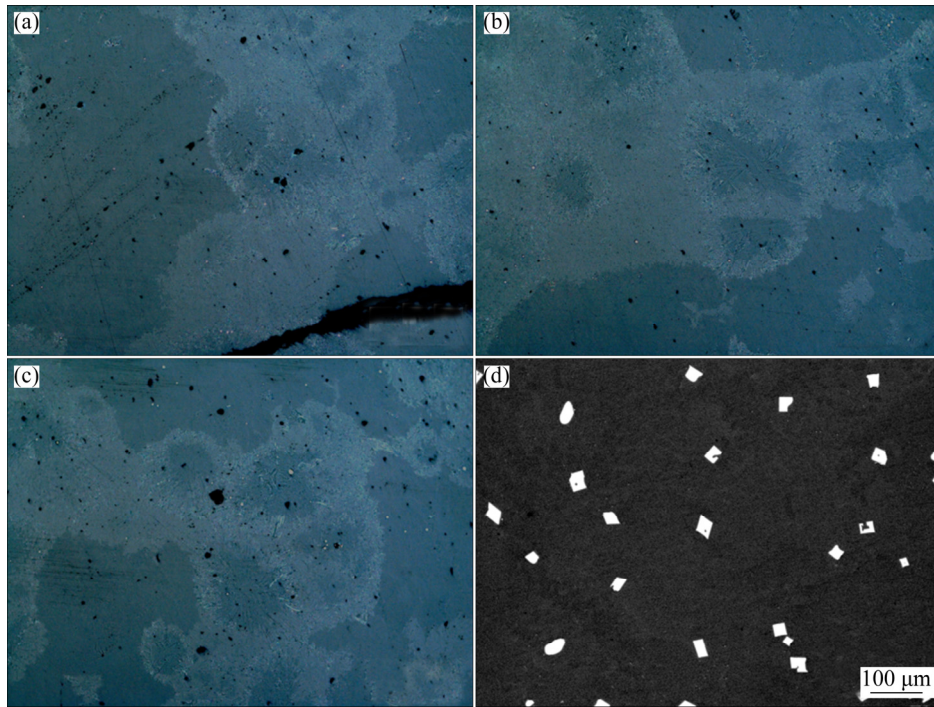
### 3.1.2 Extraction experiments of metallic iron

The effect of one-stage oxidation time on the content of metallic iron in the MTBBFS and the recovery rate of metallic iron is shown in Fig. 9(a). With one-stage oxidation time increasing from 10 to 40 s, the content of metallic irons decreased and the recovery rate of metallic iron increased. As one-stage oxidation time increased from 40 to 90 s, the content of metallic iron and the recovery rate of metallic iron remained unchanged. When one-stage oxidation time increased from 90 to 100 s, the content of metallic iron increased, while the recovery rate of metallic iron decreased. Thus, the optimal one-stage oxidation time was 40 s.

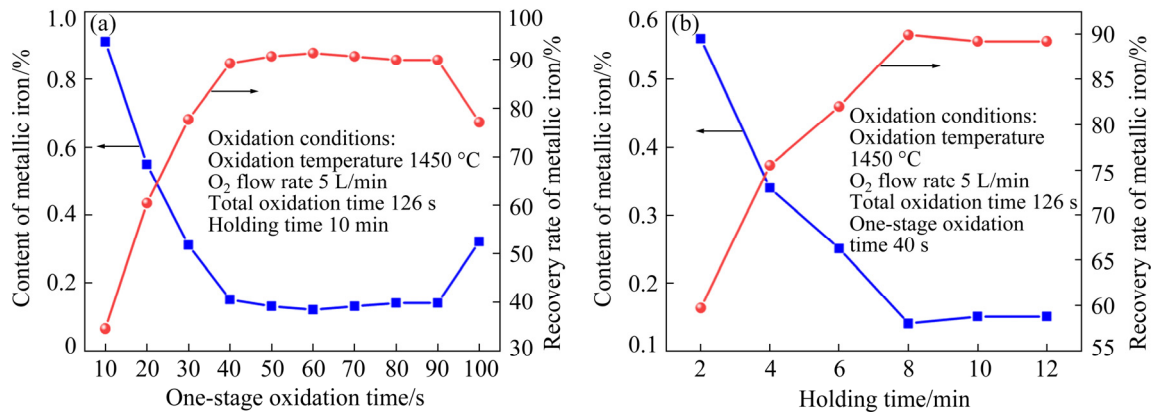
Figure 9(b) shows the effect of holding time on the content of metallic iron and the recovery rate of metallic iron. As holding time increased from 2 to 8 min, the content of metallic iron decreased and the recovery rate of metallic iron increased. With holding time increasing from 8 to 12 min, the content of metallic iron and the recovery rate of metallic iron remained unchanged. Therefore, the optimum holding time was 8 min.

The relationship between total oxidation time and viscosity is illustrated in Fig. 10. With oxidation time increasing from 0 to 42 s, the viscosity of molten slag decreased. This is because TiC and TiN in the raw materials were oxidized, leading to a decrease in the viscosity of molten slag. Thus, the recovery rate of metallic iron increased and the content of metallic iron decreased when oxidation time increased from 0 to 40 s. As oxidation time increased from 42 to 126 s, the

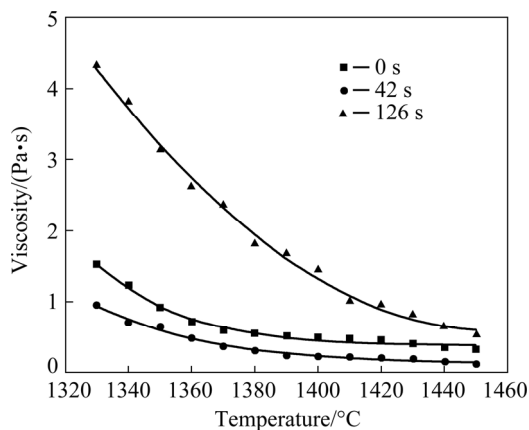




**Fig. 8** Metallographic microscope images of quenched samples with different oxidation time: (a) 0 s; (b) 42 s; (c) 84 s; (d) 126 s



**Fig. 9** Effects of one-stage oxidation time (a) and holding time (b) on content of metallic iron in MTBBFS and recovery rate of metallic iron



**Fig. 10** Relationship between total oxidation time and viscosity

viscosity of molten slag increased. This is because a large amount of rutile crystals precipitated when oxidation time was 126 s. Therefore, the recovery rate of metallic iron decreased and the content of metallic iron increased when oxidation time increased from 90 to 100 s.

In summary, the optimal experiment conditions of iron extraction were one-stage oxidation time of 40 s and holding time of 8 min. The recovery rate of iron was 89.93% and the metallic iron content of the MTBBFS was 0.14%. The chemical compositions of vanadium-containing pig iron are listed in Table 2. Table 2 reveals that the contents of Fe and V in the vanadium-containing pig iron

were 94.46 wt.% and 0.33 wt.%, respectively. The product can be used as a raw material for converter to obtain vanadium slag and semi-steel.

**Table 2** Chemical compositions of vanadium-containing pig iron (wt.%)

Fe	C	Si	V	Mn	Ti	S	P
94.46	4.31	0.35	0.33	0.28	0.14	0.072	0.058

### 3.2 Extraction of vanadium

#### 3.2.1 Extraction mechanism of vanadium

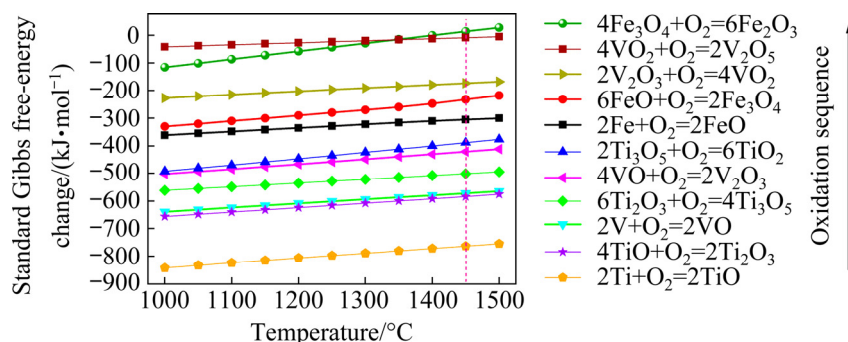
To investigate the extraction mechanism of vanadium element, the standard Gibbs free-energy changes of oxidation reactions at 1000–1500 °C were calculated, and the Pourbaix diagrams of V–Ti–H<sub>2</sub>O systems at 25 and 100 °C were drawn. The results are presented in Figs. 11 and 12. When O<sub>2</sub> is blown into molten slag, the oxidation sequence of titanium, iron, and vanadium oxides is presented in Fig. 11. At 1450 °C, it can be observed that Ti, TiO, Ti<sub>2</sub>O<sub>3</sub>, and Ti<sub>3</sub>O<sub>5</sub> are first oxidized to TiO<sub>2</sub>. In the meantime, V and VO are oxidized into V<sub>2</sub>O<sub>3</sub>. And then Fe and FeO are oxidized to Fe<sub>3</sub>O<sub>4</sub>.

Finally, V<sub>2</sub>O<sub>3</sub> and VO<sub>2</sub> are oxidized to V<sub>2</sub>O<sub>5</sub>. Since titanium slag and Ti-bearing blast furnace slag mainly contain trivalent titanium, metallic iron, and trivalent vanadium, the oxidation order is Ti<sub>2</sub>O<sub>3</sub> → Fe → V<sub>2</sub>O<sub>3</sub>.

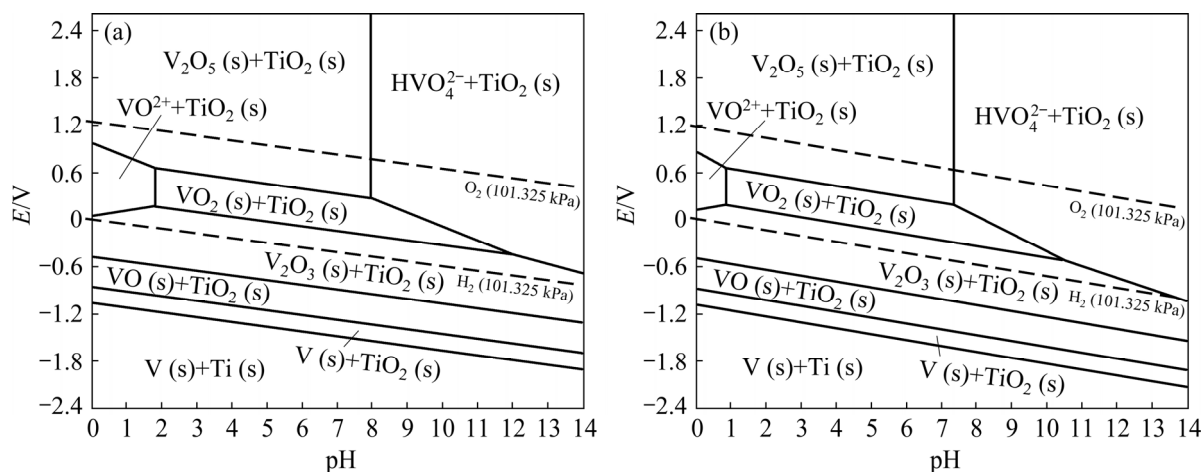
As shown in Fig. 12, VO<sub>2</sub> is leached by acid in form of VO<sup>2+</sup>. The V<sub>2</sub>O<sub>5</sub> is removed by alkali in form of HVO<sub>4</sub><sup>2-</sup>, while VO and V<sub>2</sub>O<sub>3</sub> are not leached by acid or alkali. With temperature increasing from 25 to 100 °C, the stable area of VO<sup>2+</sup> decreases, while that of HVO<sub>4</sub><sup>2-</sup> increases, implying that an increase in temperature can decrease the required pH of the alkali leaching of V<sub>2</sub>O<sub>5</sub>. It is worth noting that titanium element always exists as TiO<sub>2</sub> in the pH range of 0–14. In this work, vanadium and titanium elements in the MTBBFS are in the form of V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>, respectively. Therefore, V<sub>2</sub>O<sub>5</sub> can be leached by alkali, while TiO<sub>2</sub> is enriched in the leaching residue.

#### 3.2.2 Extraction experiments of vanadium

The effects of total oxidation time on the leaching rate of vanadium are shown in Fig. 13(a). When total oxidation time increased from 84 to



**Fig. 11** Standard Gibbs free-energy changes of oxidation reactions at 1000–1500 °C



**Fig. 12** Pourbaix diagrams of V–Ti–H<sub>2</sub>O systems at 25 °C (a) and 100 °C (b)

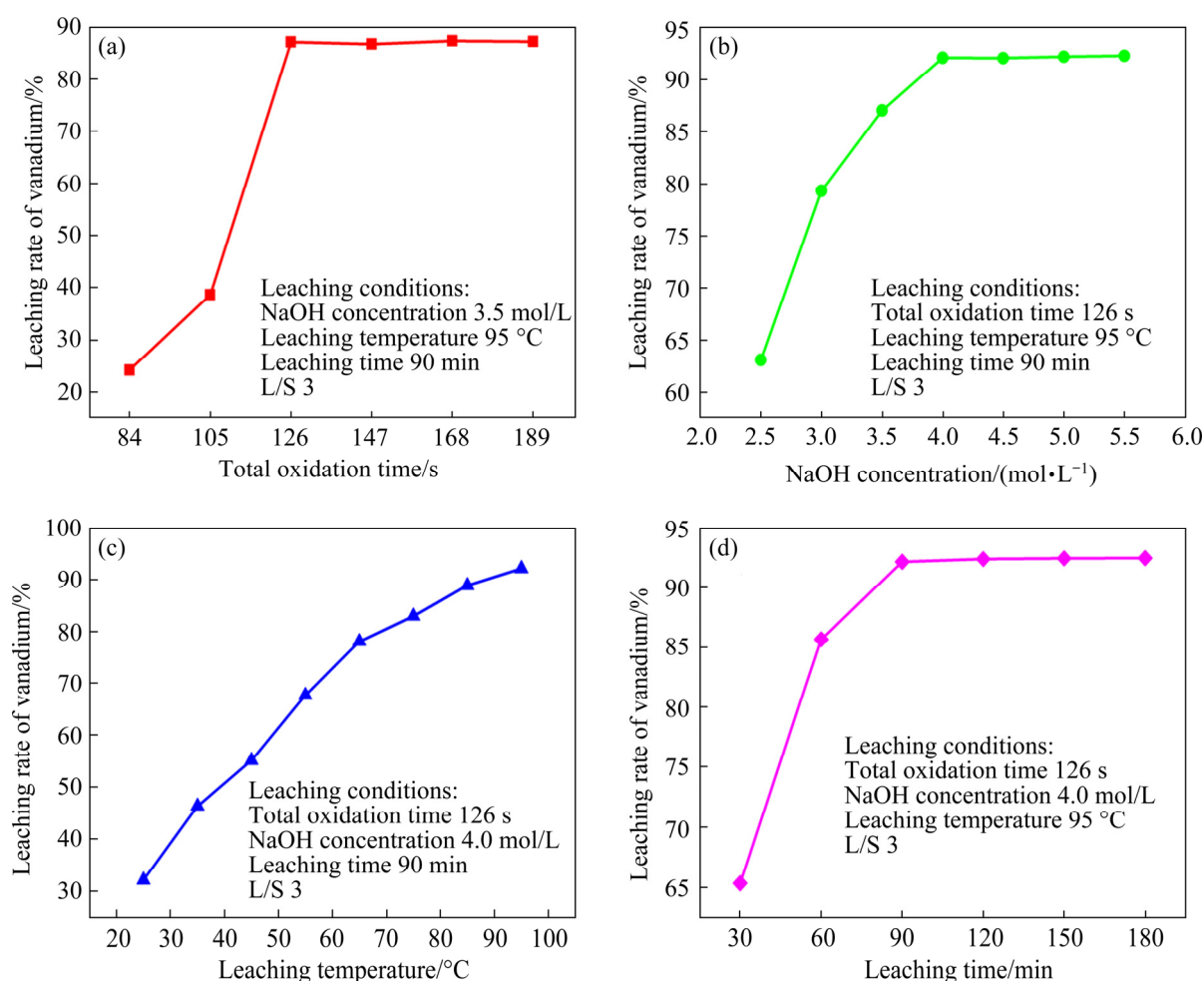


105 s, the leaching rate of vanadium slightly increased. With total oxidation time increasing from 105 to 126 s, the leaching rate of vanadium rapidly increased. It can be seen from Fig. 11 that the reason for a rapid increase is that low-valence titanium elements were first oxidized, and then low-valence vanadium elements were oxidized. As total oxidation time increased from 126 to 189 s, the leaching rate of vanadium remained unchanged. Therefore, the optimal total oxidation time was 126 s. The effects of NaOH concentration on the leaching rate of vanadium are shown in Fig. 13(b). As NaOH concentration increased from 2.5 to 4.0 mol/L, the leaching rate of vanadium significantly increased. With NaOH concentration increasing from 4.0 to 5.5 mol/L, the leaching rate of vanadium was almost constant. Thus, the optimum NaOH concentration was 4.0 mol/L. Figure 13(c) shows the effects of leaching temperature on the leaching rate of vanadium. The

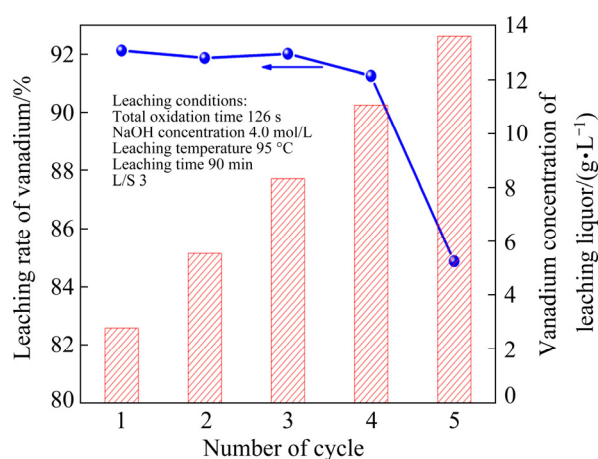
leaching rate of vanadium increased with leaching temperature increasing. Thus, the optimal leaching temperature was 95 °C. The effects of leaching time on the leaching rate of vanadium are shown in Fig. 13(d). As leaching time increased from 30 to 180 min, the leaching rate of vanadium first increased and then remained unchanged. Therefore, the optimum leaching time was 90 min.

The relationship between the number of cycle and the leaching rate of vanadium is illustrated in Fig. 14. When the number of cycle increased from 1 to 4, the leaching rate of vanadium was almost constant (about 92%) and the concentration of vanadium in leaching liquor increased. With the number of cycle increasing from 4 to 5, the concentration of vanadium continued to increase, but the leaching rate of vanadium markedly decreased. Thus, the optimal number of cycle was 4.

In summary, the optimal alkali leaching conditions were total oxidation time 126 s, NaOH



**Fig. 13** Effects of total oxidation time (a), NaOH concentration (b), leaching temperature (c), and leaching time (d) on leaching rate of vanadium



**Fig. 14** Relationship among number of cycle, leaching rate of vanadium, and vanadium concentration of leaching liquor

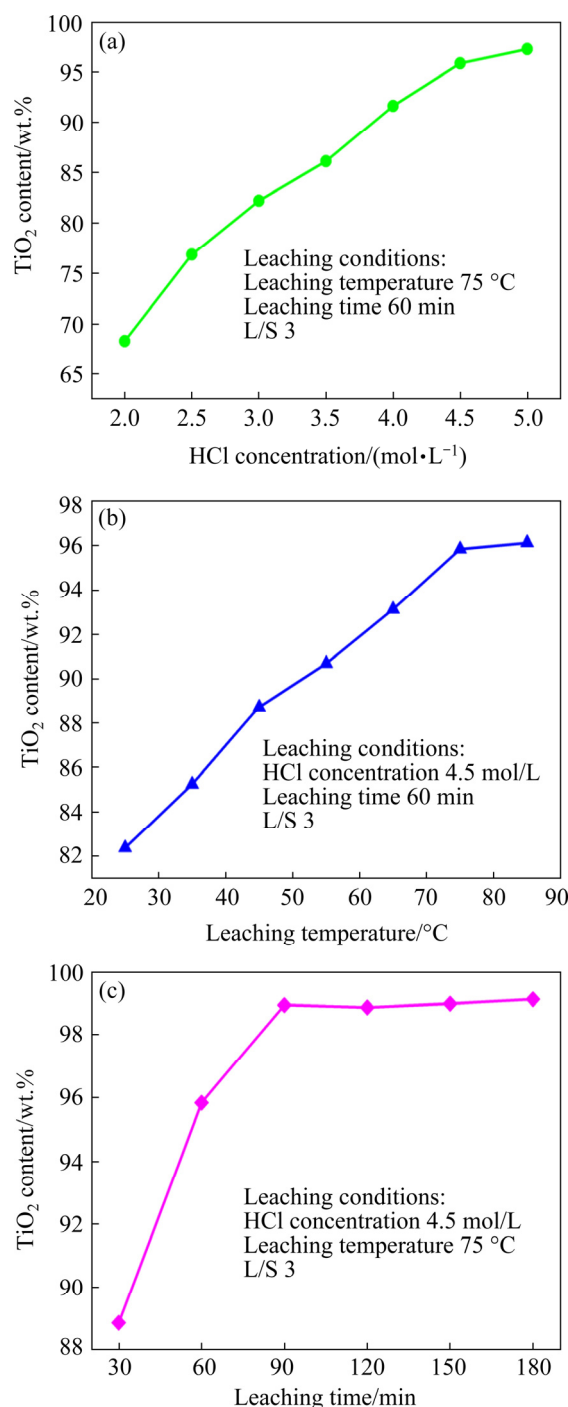
concentration 4.0 mol/L, leaching temperature 95 °C, leaching time 90 min, and the number of cycle 4. The circulating leaching solution could be used to recover vanadium by the precipitation of ammonium salt. The chemical components of the residue after alkali leaching are listed in Table 3. Table 3 reveals that the contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> are 0.29%, 0.12%, and 0.15%, respectively, implying that most SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> were leached by alkali. Therefore, the TiO<sub>2</sub> content of leaching residue increased to 72.84%.

**Table 3** Chemical compositions of residue after alkali leaching (wt.%)

TiO <sub>2</sub>	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>
72.84	0.29	19.13	0.12	6.51	0.22	0.15

### 3.3 Extraction of titanium

The effect of HCl concentration on TiO<sub>2</sub> content is shown in Fig. 15(a). As HCl concentration increased from 2.0 to 4.5 mol/L, TiO<sub>2</sub> content significantly increased. When HCl concentration increased from 4.5 to 5.0 mol/L, TiO<sub>2</sub> content slightly increased. Thus, the optimal HCl concentration was 4.5 mol/L. Figure 15(b) illustrates the effect of leaching temperature on TiO<sub>2</sub> content. With leaching temperature increasing from 25 to 75 °C, TiO<sub>2</sub> content rapidly increased. As leaching temperature increased from 75 to 85 °C, TiO<sub>2</sub> content was almost constant. Thus, the optimum leaching temperature was 75 °C. Figure 15(c) shows the effect of leaching time on TiO<sub>2</sub> content. As leaching time increased from 30 to

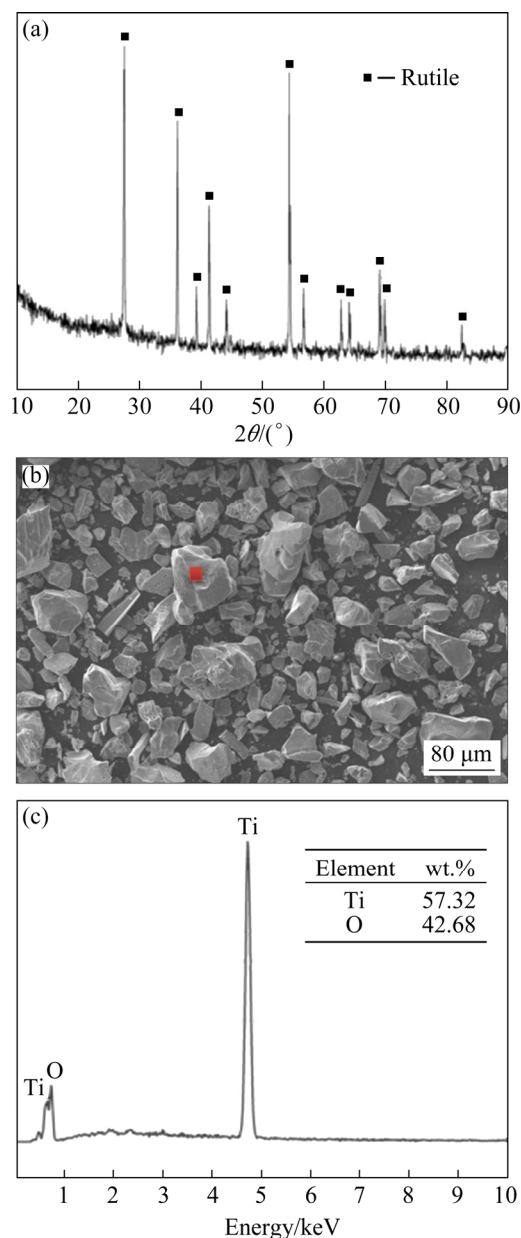


**Fig. 15** Effects of HCl concentration (a), leaching temperature (b), and leaching time (c) on TiO<sub>2</sub> content

90 min, TiO<sub>2</sub> content markedly increased. When leaching time increased from 90 to 180 min, TiO<sub>2</sub> content remained unchanged. Therefore, the optimal leaching time was 90 min.

In a word, the optimum acid leaching conditions were HCl concentration 4.5 mol/L, leaching temperature 75 °C, and leaching time 90 min. The TiO<sub>2</sub> content of synthetic rutile was 98.61%, and its total content of CaO and MgO was

0.41%. The phase and micromorphology of synthetic rutile are presented in Fig. 16. The chemical compositions of synthetic rutile are listed in Table 4. Due to the  $\text{TiO}_2$  content more than 98% and the total content of CaO and MgO less than 0.5%, the synthetic rutile was a high-quality feedstock for titanium white with the chloride process.



**Fig. 16** Characterization of synthetic rutile: (a) XRD pattern; (b) SEM image; (c) EDS analysis

**Table 4** Chemical compositions of synthetic rutile (wt.%)

$\text{TiO}_2$	$\text{SiO}_2$	CaO	$\text{Al}_2\text{O}_3$	MgO	$\text{Fe}_2\text{O}_3$	$\text{V}_2\text{O}_5$
98.61	0.32	0.24	0.07	0.17	0.15	0.19

## 4 Conclusions

(1) The optimal experiment conditions of iron extraction are one-stage oxidation time of 40 s and holding time of 8 min. The recovery rate of iron is 89.93% and the metallic iron content of the MTBBFS is 0.14 wt.%.

(2) The optimum experiment conditions of vanadium extraction are total oxidation time of 126 s, NaOH concentration of 4.0 mol/L, leaching temperature of 95 °C, leaching time of 90 min, and the number of cycle 4. The leaching rate of vanadium is 92.13%.

(3) The optimal experiment conditions of titanium extraction are HCl concentration of 4.5 mol/L, leaching temperature of 75 °C, and leaching time of 90 min. The  $\text{TiO}_2$  content of synthetic rutile is 98.61 wt.%, and the total content of CaO and MgO is 0.41 wt.%.

(4) Due to the  $\text{TiO}_2$  content more than 98 wt.% and the total content of CaO and MgO less than 0.5 wt.%, the product is a high-quality rutile for titanium white with the chloride process.

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## 改性含钛高炉渣中铁、钒和钛的回收

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**摘要:** 提出两段氧化—碱浸—酸浸工艺来回收改性含钛高炉渣中的铁、钒和钛。较佳的提铁实验条件为一段氧化时间 40 s 和保温时间 8 min, 铁的回收率为 89.93%。较佳的提钒实验条件为总氧化时间 126 s、NaOH 浓度 4.0 mol/L、浸出温度 95 °C、浸出时间 90 min 和碱浸循环次数 4, 钒的浸出率为 92.13%。较佳的提钛实验条件为 HCl 浓度 4.5 mol/L、浸出温度 75 °C 和浸出时间 90 min, 人造金红石的  $\text{TiO}_2$  含量为 98.61%。

**关键词:** 含钛高炉渣; 氧化; 改性; 浸出; 人造金红石; 生铁

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