

A novel process for the recovery of iron, titanium, and vanadium from vanadium-bearing titanomagnetite: sodium modification–direct reduction coupled process

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(Received: 19 September 2016; revised: 18 December 2016; accepted: 19 December 2016)

Abstract: A sodium modification–direct reduction coupled process was proposed for the simultaneous extraction of V and Fe from vanadium-bearing titanomagnetite. The sodium oxidation of vanadium oxides to water-soluble sodium vanadate and the transformation of iron oxides to metallic iron were accomplished in a single-step high-temperature process. The increase in roasting temperature favors the reduction of iron oxides but disfavors the oxidation of vanadium oxides. The recoveries of vanadium, iron, and titanium reached 84.52%, 89.37%, and 95.59%, respectively. Moreover, the acid decomposition efficiency of titanium slag reached 96.45%. Compared with traditional processes, the novel process provides several advantages, including a shorter flow, a lower energy consumption, and a higher utilization efficiency of vanadium-bearing titanomagnetite resources.

Keywords: titanomagnetite; direct reduction; modification; leaching; magnetic separation

1. Introduction

Vanadium-bearing titanomagnetite is a strategic resource that contains many valuable elements, including titanium, vanadium, and iron [1]. However, the complete separation of various valuable elements and comprehensive utilization of vanadium-bearing titanomagnetite have not been completely accomplished despite extensive research at home and abroad over the past several decades.

Currently, two technological processes can be used to recover valuable elements from vanadium-bearing titanomagnetite on an industrial scale. One is the blast furnace (BF) process [2], which includes multiple procedures to separate and recover iron, titanium, and vanadium. During BF smelting, titanium is concentrated in titanium slag, whereas iron and vanadium take the same orientation to vanadium-bearing molten iron. Subsequently, converter smelting is used to separate iron and vanadium. The further

extraction of vanadium from the obtained vanadium slag requires sodium roasting followed by water leaching. Even though some iron and vanadium could be recovered by the BF process, titanium slag could hardly be effectively utilized for dense structures and stable phases resulting from its exposure to a super-high-temperature environment. In addition, the relatively long flow and multiple high-temperature procedures resulted in relatively long production circle and high energy consumption, which degraded the attractiveness of the BF process in the field of comprehensive utilization of vanadium-bearing titanomagnetite. Furthermore, the depletion of coke in the BF process further necessitated the development of an alternative process. In this context, the direct reduction–electric furnace smelting (DR–EF) process [3–12] emerged and has been preliminary employed in industry.

The DR–EF process also consists of multiple procedures such as direct reduction, usually by a rotary hearth furnace, electric furnace smelting, converter smelting, and sodium

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roasting. Titanium is concentrated in titanium slag, and iron and vanadium enter simultaneously into vanadium-bearing molten iron after direct reduction followed by electric furnace smelting. The vanadium-bearing molten iron is also subjected to several procedures such as converter smelting, sodium roasting, and water leaching to separate and recover iron and vanadium. Although the recoveries of iron and vanadium are slightly increased in comparison with the BF process, problems such as the long production circle, high energy consumption, high cost, and waste of titanium still exist. Consequently, the development of a novel process for the comprehensive utilization of vanadium-bearing titanomagnetite is urgently needed.

In the present work, a novel process — the sodium modification–direct reduction coupled (SRC) process — was proposed and investigated for the comprehensive utilization of vanadium-bearing titanomagnetite. In the roasting process, the direct reduction for reducing iron oxides to metallic iron and the sodium roasting for transforming vanadium oxides to water-soluble sodium vanadate were accomplished simultaneously at relatively low roasting temperatures. This process represents an important original technological innovation in the field of multipurpose utilization of vanadium-bearing titanomagnetite.

2. Experimental

2.1. Materials

Vanadium-bearing titanomagnetite concentrates were obtained from the Panxi region, China. X-ray diffraction (XRD, Smartlab-9 X-ray diffractometer, Rigaku, Japan) and scanning electron microscopy (SEM, Quanta 250-GENESIS XM 2i, FEI, USA) in conjunction with electron-probe microanalysis (EPMA, 1720H, Japan) were jointly used to determine the species of iron, titanium, and vanadium in the concentrates. According to the XRD pattern shown in Fig. 1,

the SEM image shown in Fig. 2, and the elemental analysis results for micro-areas shown in Table 1, iron and titanium mainly exist as magnetite (Fe_3O_4), titanomagnetite ($\text{Fe}_{2.25}\text{Ti}_{0.75}\text{O}_4$), and ilmenite (FeTiO_3), whereas vanadium mainly exists in the form of vanadium–iron spinel (FeV_2O_4). The chemical compositions of the concentrates and the industrial analysis of anthracite are listed in Tables 2 and 3, respectively. All the chemical reagents were analytical grade.

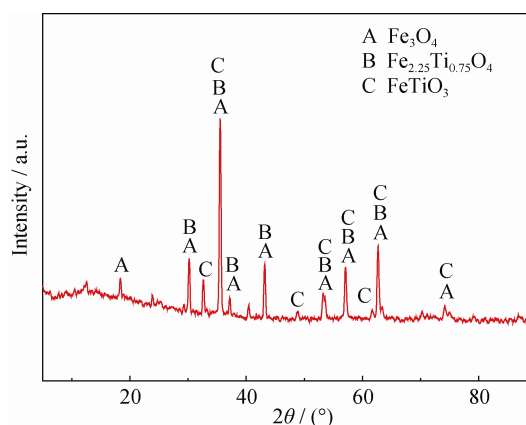


Fig. 1. XRD pattern of vanadium-bearing titanomagnetite used in the experiments.

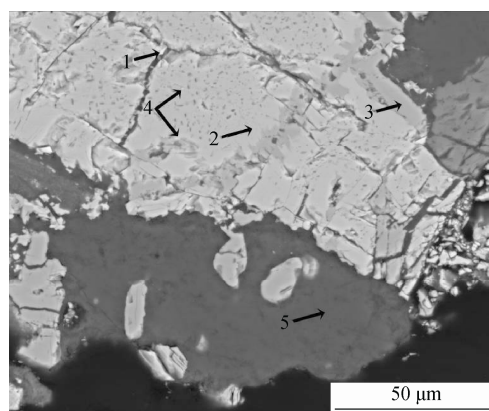


Fig. 2. SEM image of vanadium-bearing titanomagnetite.

Table 1. Composition analysis results for points 1–5 in Fig. 2

Locations	Phases	Fe	Ti	O	V	Ca	Mg	Al	Si	wt%
1	Fe_3O_4	70.480 (1.262)	—	29.520 (1.845)	—	—	—	—	—	—
2	$\text{Fe}_{2.25}\text{Ti}_{0.75}\text{O}_4$	55.590 (0.995)	13.970 (0.292)	30.440 (1.903)	—	—	—	—	—	—
3	FeTiO_3	36.040 (0.645)	31.690 (0.662)	32.270 (2.017)	—	—	—	—	—	—
4	FeV_2O_4	25.790 (0.462)	—	27.120 (1.695)	46.900 0.963	—	—	—	—	—
5	silicates	2.280 (0.041)	—	41.590 (2.599)	—	—	23.360 (0.961)	13.300 (0.493)	19.470 (0.695)	—

Note: The values in parentheses are the amount of substances, mol.

Table 2. Chemical composition of vanadium-bearing titanomagnetite

								wt%
TFe	FeO	TiO ₂	V ₂ O ₅	MnO	CaO	MgO	Al ₂ O ₃	SiO ₂
51.37	25.48	13.66	0.53	0.30	1.16	3.24	2.86	3.83

Table 3. Industrial analysis of anthracite

				wt%
Moisture	Ash	Volatiles	Fixed carbon	
2.08	8.65	3.98	85.29	

2.2. Experimental procedure

2.2.1. SRC process

The vanadium-bearing titanomagnetite concentrates were first crushed and ground to 65wt% passing 74 μm. Afterwards, 50 g of the concentrates was mixed homogeneously with 16wt% pulverized anthracite and 35wt% sodium carbonate. The mixture was subsequently placed into a graphite crucible (Jinda Factory, China) with a lid. The samples were heated in an electric muffle furnace (CNT Furnace Factory, China) at the desired temperature from 950 to 1200°C. The isothermal process was conducted for 2 h, and then the crucible was removed from the furnace. After the sample cooled to room temperature under an inert atmosphere, the roasted products were crushed and ground to be smaller than 74 μm. The chemical compositions of the roasted products were determined by inductively couple plasma optical emission spectroscopy (ICP-OES, Optical 5300DV, Perkin Elmer, USA).

2.2.2. Extraction process of vanadium

The vanadium was extracted from the roasted products via a water leaching process. The water-leaching experiments were carried out in a 0.5-L, three-necked, round-bottom flask with a Teflon-coated stirrer. The roasted products were first mixed with deionized water (L/S = 5:1 mL/g). The resulting mixture was heated in an oil bath at a preset temperature of 90°C for 2 h. The leaching residue was then collected by filtration using a vacuum air pump and subsequently dried in a vacuum drying chamber. The vanadium content in the leaching residues was then analyzed via ICP-OES. The leaching efficiencies of V were calculated according to Eq. (1):

$$\text{Leaching efficiency of vanadium} = \left(1 - \frac{W_1}{W_r}\right) \times 100\% \quad (1)$$

where W_r and W_1 are the mass percentages of vanadium in the roasted product and in the leaching residue, respectively.

2.2.3. Separation process of iron and titanium

The iron and titanium were separated via a magnetic separation process. After the water leaching experiment, the leaching residue was treated by wet-milling in a stainless steel rod mill with hardened stainless steel rods for 30 min.

The milled samples were then separated by a low-intensity magnetic separator with a magnetic field intensity of 60 kA/m. The magnetic and nonmagnetic components were then collected separately by filtration using a vacuum air pump and dried in a vacuum drying chamber. The chemical compositions of the magnetic iron concentrates and nonmagnetic titanium slag were then determined via ICP-OES. The recoveries of iron and titanium were calculated according to Eq. (2):

$$\text{Recovery of iron or titanium} = \frac{I_m}{I_r} \times 100\% \quad (2)$$

where I_m is the mass of iron in the magnetic iron concentrates or titanium in the nonmagnetic titanium slag, and I_r is the mass of iron or titanium in the roasted products.

2.2.4. Acid decomposition process of titanium slag

The titanium concentrated in titanium slag was extracted via acid decomposition and subsequent acid leaching processes, which were conducted using glass round-bottom flasks in a temperature-controlled oil bath. Titanium slag was first digested with sulfuric acid (95wt%) for 2 h at 190°C. The H₂SO₄-to-TiO₂ mass ratio was 1:1. The obtained decomposition product was then leached with 2vol% H₂SO₄ for 3 h at 65°C. The H₂SO₄-to-TiO₂ mass ratio was 5:1. The concentration of TiO₂ in the leaching liquor was determined by ICP-OES. The acid decomposition efficiency of titanium slag was calculated according to Eq. (3):

$$\text{Decomposition efficiency of titanium} = \left(1 - \frac{M_s}{M_{\text{slag}}}\right) \times 100\% \quad (3)$$

where M_s and M_{slag} are the mass of TiO₂ in the acid leaching residue and that in the titanium slag, respectively.

3. Results and discussion

3.1. Why can the direct reduction of FeO_x and the sodium oxidation of VO_x be accomplished simultaneously?

The SRC process was first analyzed using a thermodynamic calculation method. According to the calculation results shown in Fig. 3, the direct reduction of iron oxides, including Fe₃O₄ and FeTiO₃, and the oxidation with sodium activation of FeV₂O₄ can occur simultaneously in the temperature range from 720 to 1200°C. Moreover, the oxidation and sodium activation of FeV₂O₄ is thermodynamically favored over the gasification of carbon. That is, the oxidation

of V^{3+} to V^{5+} has already reached a terminal point before the gasification of carbon, which transforms the environment in the furnace from an oxidizing atmosphere to a reducing atmosphere. Furthermore, according to line (7) in Fig. 3, the obtained $NaVO_3$ remains stable when the temperature is less than $1200^\circ C$. Generally, the transformation of iron oxides to metallic iron and vanadium oxides to water-soluble sodium vanadate can be achieved simultaneously in a one-step roasting process as long as the roasting temperature is in the range from 720 to $1200^\circ C$.

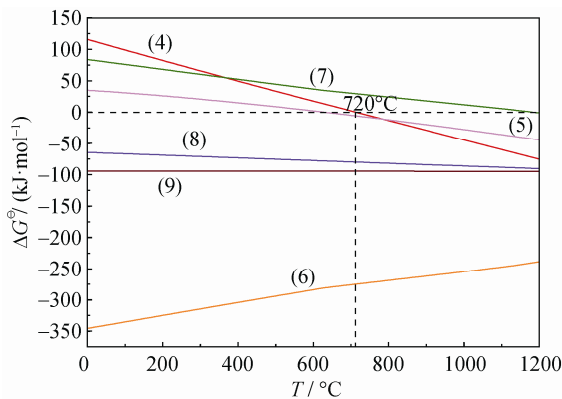
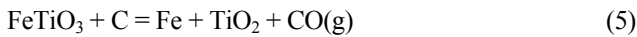
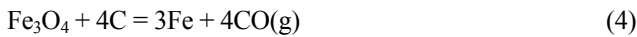
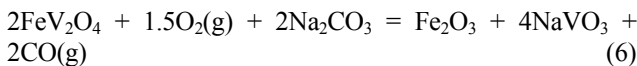


Fig. 3. Thermodynamic analysis of the SRC process.

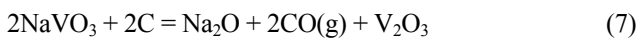
Iron oxides are reduced as



FeV_2O_4 is oxidized as



The reduction of sodium vanadate occurs via the reaction



And the gasification of carbon occurs as



3.2. Extraction of vanadium

After the mixture of vanadium-bearing titanomagnetite, pulverized anthracite, and sodium carbonate was roasted at a high temperature, the roasted products were leached using water to extract vanadium. The effect of roasting temperature on the leaching efficiency of V is shown in Fig. 4, which reveals that the leaching efficiency of vanadium decreased from 94.27% to 86.21% as the roasting temperature was increased from 950 to $1200^\circ C$. The standard Gibbs free energy (ΔG^\ominus) values for the oxidation reactions of vanadium oxide increase and finally tend toward zero when the temperature increases from 950 to $1200^\circ C$, especially for the oxidation of $V(IV)$ to $V(V)$ [13]. The increasing difficulty in the oxidation of vanadium oxide might be responsi-

ble for the decrease of vanadium leaching efficiency with increasing roasting temperature.

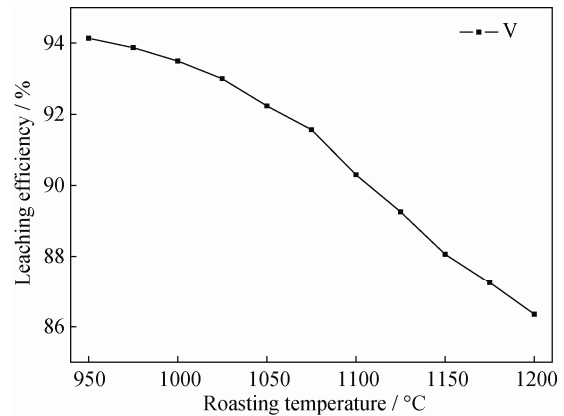


Fig. 4. Effect of roasting temperature on the leaching efficiency of vanadium.

To further verify the oxidation of vanadium during the roasting process, X-ray photoelectron spectroscopy (XPS) was used to analyze the vanadium-bearing titanomagnetite and the roasted product to determine the valence state of vanadium. Because the binding energy of the $V2p_{3/2}$ core level depends on the oxidation state of the V cation, curve fitting of the $V2p_{3/2}$ XPS spectrum can be used to detect the different oxidation states of vanadium cations. On the basis of the vanadium spectra of the vanadium-bearing titanomagnetite (Fig. 5(a)) and the roasted products (Fig. 5(b)), most of the V^{3+} in the vanadium-bearing titanomagnetite is oxidized to V^{5+} during the roasting process. Moreover, according to the phase compositions (Fig. 6), elemental compositions (Table 4), and chemical compositions (Table 5) of the roasted product and water leaching residue, vanadium was successfully extracted from the roasted product into the water leaching liquor via the water leaching process. Generally, vanadium oxides were successfully transformed from vanadium-bearing titanomagnetite to water-soluble sodium vanadate with V^{5+} via the roasting process.

3.3. Separation of iron and titanium

After the water leaching process, the water leaching residue was used to separate and recover iron and titanium using a magnetic separation method. The effect of roasting temperature on the recoveries of iron and titanium and on the iron grade in the iron concentrates is shown in Fig. 7, which reveals that the recoveries of iron and titanium and the iron grade in iron concentrates increase with increasing roasting temperature. Specifically, the increase in roasting temperature favors the separation and recovery of iron and titanium. After the magnetic separation process, most of the

iron was concentrated in magnetic substances and most of the titanium entered into nonmagnetic substances. The com-

plete separation of metallic iron and titanium slag was nearly achieved.

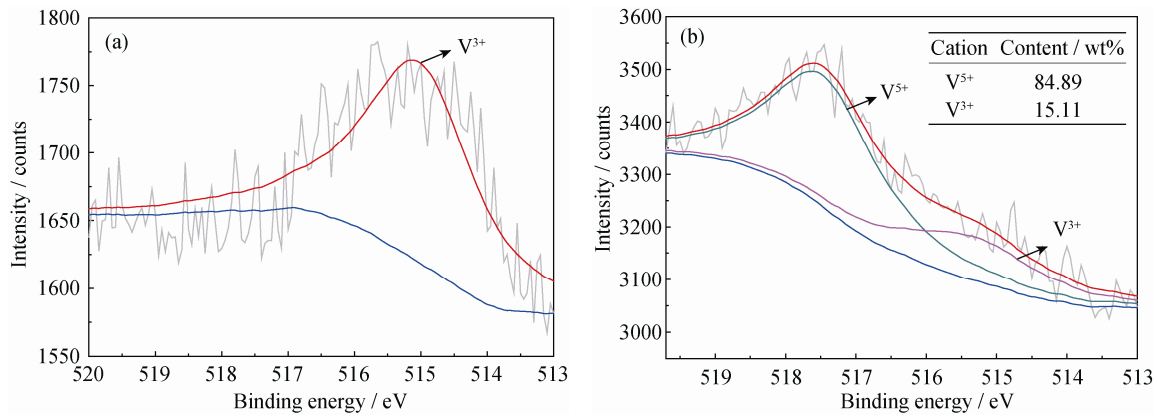


Fig. 5. XPS spectra of $V2p_{3/2}$ of the vanadium-bearing titanomagnetite (a) and the product roasted at 1200°C (b).

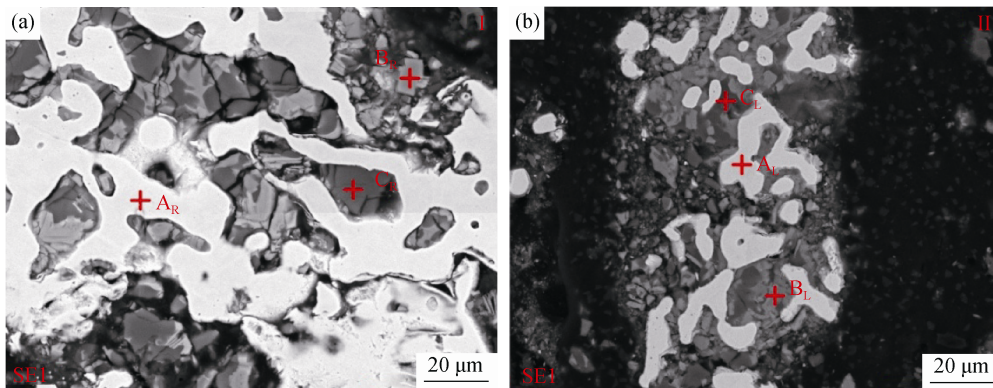


Fig. 6. Analysis of the morphology and elemental composition of the roasted product obtained at 1200°C (a) and the water leaching residue (II).

Table 4. Elemental contents of different phases shown in Fig. 6

wt%

Sample	Phase	Elemental contents									
		Fe	Ti	V	Ca	Mg	Al	Si	O	C	Na
Roasting products	A _R	97.35	0	0	0	0	0	0	0	2.65	0
	B _R	10.67	5.27	0.40	0	0.40	22.91	11.30	35.41	—	13.64
	C _R	0.69	8.70	0.02	0.44	2.40	12.10	17.36	42.31	—	15.98
Leaching residue	A _L	97.67	0	0	0	0	0	0	0	2.33	0
	B _L	6.04	29.16	0.01	0	0.35	5.15	5.88	49.03	—	5.36
	C _L	9.34	32.84	0.02	0.46	2.52	2.35	3.89	41.95	—	6.63

To verify the reduction of iron oxides and the effective separation of iron and titanium after roasting and magnetic separation processes, the phase compositions of roasted products, iron concentrates, and titanium slag were determined by XRD. The results are shown in Fig. 8, which indicates that the titanomagnetite, magnetite, and ilmenite in the vanadium-bearing titanomagnetite were reduced to metallic iron and a small amount of ferrous oxide during the

roasting process. The titanium present in minerals including titanomagnetite and ilmenite in the concentrates was released and reacted with other substances such as sodium carbonate, magnesium oxide, and calcium oxide to produce $\text{Na}_{0.66}\text{Mg}_{0.34}\text{Ti}_{0.66}\text{O}_2$, Mg_2TiO_4 , and CaTiO_3 during the roasting process. The iron concentrates obtained through magnetic separation were mainly composed of metallic iron, which could be directly used in the steelmaking industry.

The titanium slag obtained by magnetic separation consisted of titanium-bearing minerals such as $\text{Na}_{0.66}\text{Mg}_{0.34}\text{Ti}_{0.66}\text{O}_2$ and CaTiO_3 , silicates such as $\text{Na}_{1.74}\text{Mg}_{0.865}\text{Si}_{1.13}\text{O}_4$ and $\text{Na}_{1.75}\text{Al}_{1.75}\text{Si}_{0.25}\text{O}_4$, and a small amount of FeO . In addition, according to the chemical compositions of the different products listed in Table 5, most of the iron and titanium were separately concentrated in iron concentrates and titanium slag. Generally, both the reduction of iron oxides to metallic iron during the roasting process and the separation of metallic iron and titanium slag during the magnetic separation process were well accomplished.

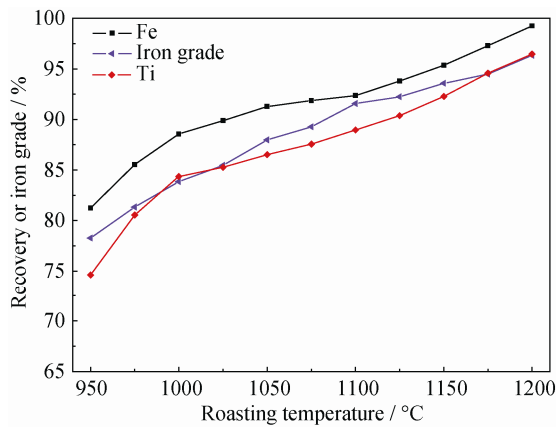


Fig. 7. Effect of roasting temperature on the recovery of iron and titanium.

3.4. Acid digestion of titanium slag

After the magnetic separation process, the obtained titanium slag was used to extract titanium via the H_2SO_4 decomposition method. The chemical compositions of titanium slag and the obtained titanyl sulfate solution are shown in Tables 5 and 6, respectively. After the acid decomposition process, the decomposition efficiency of titanium could reach 96.45%. Moreover, the concentration of titanium oxides in titanyl sulfate solution could reach 123 g/L, which indicates that the solution can be used to produce titanium dioxide in industry.

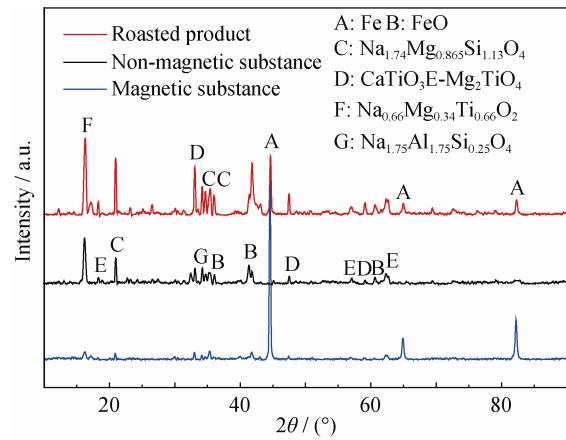


Fig. 8. XRD patterns of different products.

Table 5. Chemical composition of different products

Sample	TFe	MFe	TiO ₂	V ₂ O ₅	MnO	CaO	MgO	Al ₂ O ₃	SiO ₂	wt%
Roasted product	47.14	—	13.37	0.55	0.32	1.30	5.34	7.56	10.60	
Water-leaching residue	50.14	—	16.45	0.01	0.43	1.68	5.97	6.97	10.39	
Iron concentrates	90.42	89.79	2.17	0.07	0.09	0.46	2.07	2.08	3.47	
Titanium slag	9.22	—	35.85	0.02	0.58	2.65	5.75	7.05	12.30	

Table 6. Chemical composition of the titanyl sulfate solution obtained by H₂SO₄ decomposition

Chemical composition	TiO ₂	H ₂ SO ₄	Fe	V	Ca	Mg	Al	Mn	Si
Concentration / (g·L ⁻¹)	123.0	246.9	0.97	0.02	1.5	0.15	0.48	0.18	0.83

3.5. Novelty of the SRC process

3.5.1. Shorter flow

The flow sheets of the SRC process, BF process, and DR-EF process for vanadium-bearing titanomagnetite are shown in Figs. 9–11, respectively. Obviously, traditional comprehensive utilization processes for vanadium-bearing titanomagnetite require several procedures to separate and recover valuable elements. The BF process mainly includes five procedures: pelletization or sintering, BF smelting, converter smelting, sodium roasting, and water leaching. The DR-EF process mainly includes five procedures: direct reduction by rotary hearth furnace, electric furnace smelting,

converter smelting, sodium roasting, and water leaching. However, the SRC process proposed in this work only includes three procedures: sodium modification–direct reduction, water leaching, and magnetic separation. Consequently, the SRC process is much shorter than traditional processes, which could greatly shorten the production cycle and lower operating costs.

3.5.2. Lower energy consumption

As shown in Fig. 10, the BF process includes three high-temperature procedures: BF smelting at 1500–1600°C, converter smelting at 1650°C, and sodium roasting at 850°C. As shown in Fig. 11, the DR-EF process includes four high-temperature procedures: direct reduction by a rotary

hearth furnace at 1350°C, electric furnace smelting at 1600°C, converter smelting at 1650°C, and sodium roasting at 850°C. However, the SRC process only includes one high-temperature procedure: sodium modification–direct reduction at 1200°C. The substantial reduction of high-temperature procedures and the relatively low temperature should result in a substantial decrease in energy consumption.

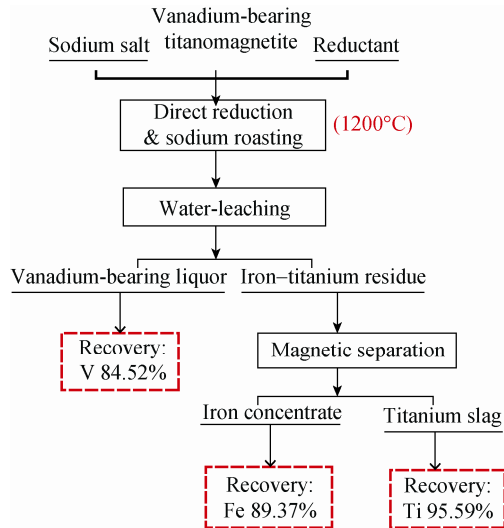


Fig. 9. Flow sheet of the SRC process for vanadium-bearing titanomagnetite.

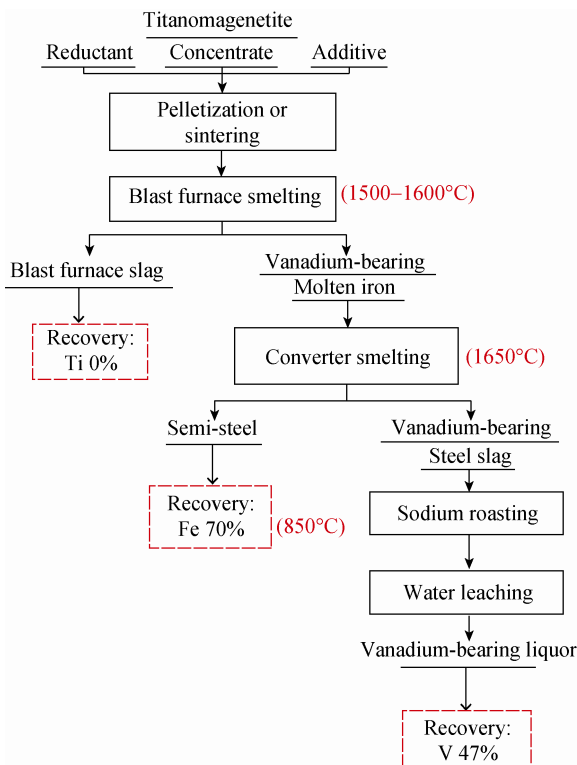


Fig. 10. Flow sheet of the BF process for vanadium-bearing titanomagnetite.

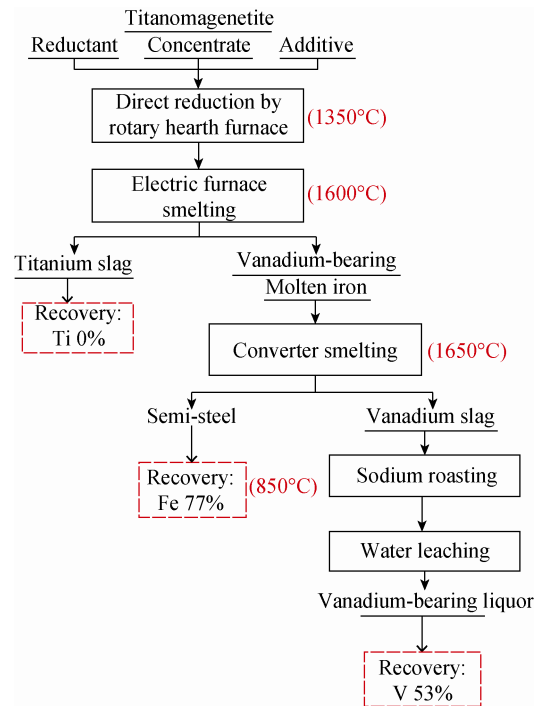


Fig. 11. Flow sheet of the DR-EF process for vanadium-bearing titanomagnetite.

3.5.3. Higher utilization efficiency of resources

In the BF process, approximately 70% iron and 47% vanadium could be separately recovered from vanadium-bearing titanomagnetite. In the DR-EF process, the recoveries of iron and vanadium are 77% and 53%, respectively. However, the recoveries of iron and vanadium could reach 84.52% and 89.37% via the SRC process, respectively. Obviously, the recoveries of iron and vanadium were greatly increased by the SRC process.

In addition, even though some iron and vanadium from vanadium-bearing titanomagnetite could be effectively recovered and utilized by the traditional BF process and the DR-EF process, the utilization efficiency of titanium approximates zero for the stable phases in the titanium slag obtained by high-temperature processes such as BF smelting at 1500–1600°C and electric furnace smelting at 1600°C [14–18]. However, in the SRC process, the titanium-bearing phases would be subjected to a one-step roasting process at a relatively low temperature of 1200°C, thereby avoiding high-temperature BF smelting or electric furnace smelting processes, which is favorable for the effective utilization of titanium slag in the industrial production of titanium dioxides.

4. Conclusions

In this study, a novel method named the sodium modifi-

cation–direct reduction coupled process was proposed for recovering iron, titanium, and vanadium from vanadium-bearing titanomagnetite. In the roasting process, the reduction of iron oxides to metallic iron and sodium oxidation of vanadium oxides to water-soluble sodium vanadate were simultaneously accomplished. After subsequent water leaching and magnetic separation processes, vanadium, iron, and titanium were recovered into vanadium-bearing water leaching liquors, iron concentrates, and titanium slag, respectively. In addition, the iron concentrates obtained by magnetic separation could be directly used in the steelmaking industry. The vanadium-bearing water-leaching liquor could be used to prepare vanadium-bearing products. Titanium slag could be utilized in the industrial production of titanium dioxides. Compared with traditional processes, this novel process offers several advantages, including shorter flow, lower energy consumption, and high utilization efficiency of resources; it also provides a novel prospect for the comprehensive utilization of vanadium-bearing titanomagnetite.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (Nos. 2013CB632601 and 2013CB632604), the National Science Foundation for Distinguished Young Scholars of China (Nos. 51125018 and 51504230), the Key Research Program of Chinese Academy of Sciences (No. KGZD-EW-201-2), the National Natural Science Foundation of China (Nos. 51374191 and 2110616751104139), and China Postdoctoral Science Foundation (Nos. 2012M510552 and 2013T60175).

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