



Direct carbothermic reduction of ilmenite concentrates by adding high dosage of Na_2CO_3 in microwave field

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Abstract: A clean and efficient route for the utilization of ilmenite concentrates was proposed by direct carbothermic reduction in microwave field. High dosage of Na_2CO_3 , which can be recycled, was added to accelerate the reduction reaction of ilmenite concentrates. After microwave heating in the temperature range of 1073–1123 K for 20 min, the main products were Na_2TiO_3 and metallic Fe with the metallization ratios being as high as 92.67%–93.21%. The reduction products were processed by water leaching, ball-milling in CO_2 atmosphere and magnetic separation in turn. The final products after magnetic separation were Fe-rich materials and Ti-rich materials (90.04 wt.% TiO_2), which can be used to produce iron and TiCl_4 or TiO_2 . The optimized heating temperature was 1123 K in terms of metallization ratios, magnetic separation and caking property of the reduction products. Besides, the reduction mechanism of ilmenite concentrates with the addition of Na_2CO_3 in microwave field was also proposed.

Key words: ilmenite concentrates; microwave; Na_2CO_3 ; carbothermic reduction

1 Introduction

Ilmenite is a kind of complex mineral containing both iron and titanium, which is of vital importance in metallurgical industry [1,2]. However, there is no clear and efficient route to produce iron and TiO_2 pigment directly at present. Chlorination process is not a suitable method due to the low-grade TiO_2 and high impurity of ilmenite concentrates [3,4]. Sulfate process seems to be an efficient route to produce TiO_2 pigments [5], but it is restrained by the severe environmental challenge [6,7]. Conventional blast furnace route requires high temperature, which is difficult to extract TiO_2 from the produced Ti-rich slags [8]. Many researchers [9–12] have investigated the gas-based reduction of ilmenite. However, there is still a

long way for the industrialization of gas-based reduction of ilmenite due to the shortage of cheap gas. Solid-state reduction of ilmenite [13–19] is a promising method to obtain iron and TiO_2 pigment at relatively low temperatures. However, it is time-consuming with the reduction time being around 2–3 h in general.

As a clean and efficient process for the preparation of materials, microwave techniques attracted considerable attentions in recent years [20–24]. Many researchers [18,25–29] have proven that ilmenite concentrates had excellent microwave-absorbing characteristics, which could be heated up quickly in microwave field. KELLY and ROWSON [29] investigated the utilization of microwave energy for the reduction of oxidized ilmenite concentrates in a time-saving and energy-saving way. LI et al [18] found that iron was formed

in the reduction of ilmenite at 1173 K in microwave field, which is lower than the reduction temperature by conventional electric furnace heating. Therefore, microwave heating is benefit for the solid-state reduction of ilmenite.

Additives can intensify the reduction of ilmenite. However, the amount of additives is normally below 5 wt.% due to the restraint of caking problem [16–18,30,31]. In conventional heating process, the caking problem is difficult to be avoided due to the long heating-time and high heating-temperature. However, in microwave heating process, it is possible to control the caking problem of additives due to the fast and efficient heating characteristics of microwave.

In the present work, a direct carbothermic reduction method of ilmenite concentrates was investigated by adding high dosage of Na_2CO_3 in microwave field. The caking problems of the reduction products could be controlled by microwave irradiation due to the low heating temperature and short reduction time.

2 Experimental

2.1 Materials

The ilmenite concentrates used in this investigation were supplied by Panzhihua Iron and Steel Company (Panzhihua, China). The main chemical composition is presented in Table 1. The graphite (≥ 99.8 wt.%) and Na_2CO_3 (≥ 99.8 wt.%) were supplied by Sino Pharm Chemical Reagent Co., Ltd.

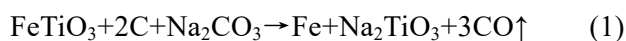
Table 1 Chemical compositions of ilmenite concentrates (wt.%)

TFe	TiO ₂	SiO ₂	CaO	MgO	Al ₂ O ₃	V ₂ O ₅	MnO
33.58	44.92	1.18	1.37	3.12	2.47	0.07	0.65

2.2 Instrument and procedures

The schematic diagrams of microwave heating apparatus (3 kW and 2.45 GHz) and conventional heating instrument are illustrated in Fig. 1.

The reduction reaction is given in the following equation:



The process flowsheet for direct carbothermic reduction of ilmenite concentrates is illustrated in Fig. 2. First, the ilmenite (FeTiO_3) was mixed with

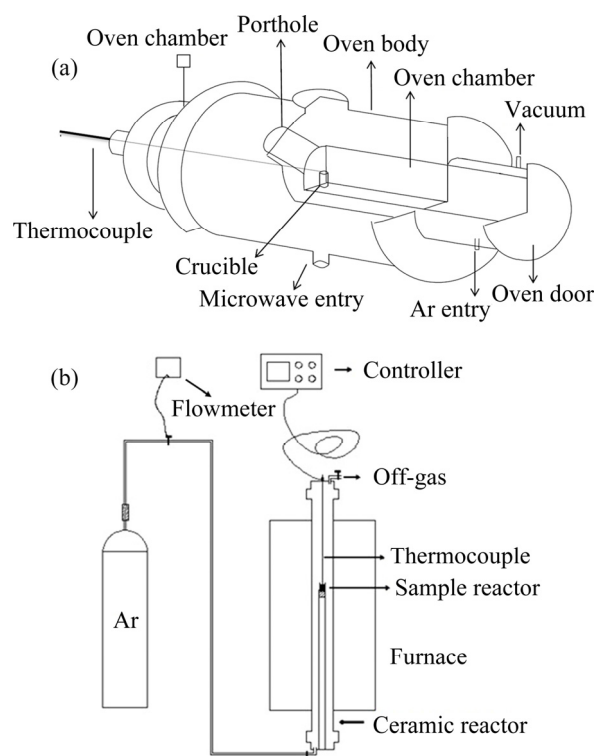


Fig. 1 Schematic diagrams of heating apparatus: (a) Microwave oven; (b) Electric oven

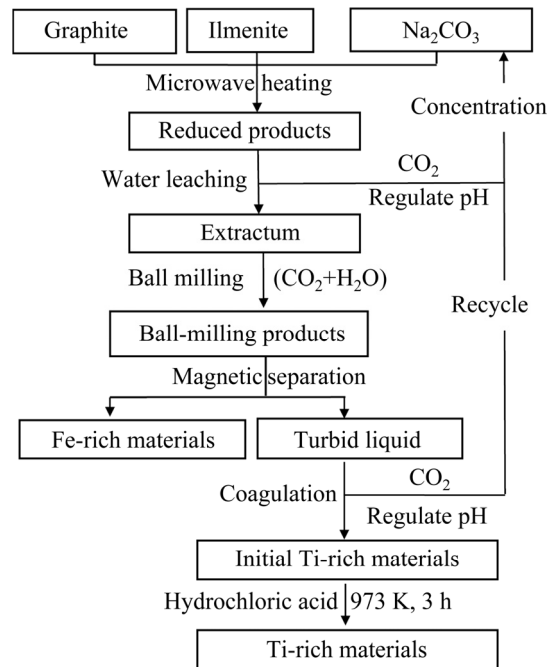


Fig. 2 Flowsheet of new route

graphite (C) and Na_2CO_3 with larger mole ratios than the stoichiometric ratios by ball-milling for 2 h. The chemical compositions of the samples are listed in Table 2. The molar ratios of Na_2CO_3 and C in Table 2 were determined by the molar ratio of FeTiO_3 , which were set as 1 mol according to

Table 2 Chemical compositions of samples

Sample No.	Molar ratio			Composition/wt.%		
	FeTiO ₃	NaCO ₃	C	FeTiO ₃	NaCO ₃	C
1 (0Na ₂ CO ₃ –2.8C)	1	0	2.8	0.82	0.00	0.18
2 (0Na ₂ CO ₃ –8C)	1	0	8	0.61	0.00	0.39
3 (0.5Na ₂ CO ₃ –2.8C)	1	0.5	2.8	0.64	0.22	0.14
4 (1.4Na ₂ CO ₃ –2.8C)	1	1.4	2.8	0.45	0.44	0.10

Eq. (1). In order to investigate the effect of Na₂CO₃, two samples with more C (0Na₂CO₃–8C) and less Na₂CO₃ (0.5Na₂CO₃–2.8C) than the stoichiometric ratios were also prepared under the same condition for comparison.

All the samples were placed in a BN crucible and heated up to certain temperatures under Ar gas in a tube microwave furnace, and all the samples can be heated up to the target temperatures (1023–1173 K) within 10 min, which indicates the good microwave heating property of the mixtures. The purity of the gas used in the investigation was 99.999 wt.%. The reduction products were processed with the steps shown in Fig. 2 to produce Ti-rich and Fe-rich materials.

2.3 Analytical method

The phases of the reduction products were characterized by X-ray diffraction analysis (XRD, Bruker AXS, D8 Advance, Cu K_α radiation, 40 kV and 40 mA). Microscopic observation and analysis for the reduced samples were conducted by scanning electron microscope and energy dispersive spectroscopic (SEM and EDS, HITACHI SU–1500, HITACHI, Japan). The contents of Ti and Fe in Ti-rich and Fe-rich materials were determined by ICP-OES (Perkin-Elmer 7300DV, America). The chemical compositions of samples were determined by X-ray fluorescence (XRF, XRF–1800, Shimadzu, Kyoto, Japan). The total Fe (T_{Fe}) and metallic Fe (M_{Fe}) contents in the reduction products were determined by titrimetric analyses for four times, respectively. The metallization ratios (γ) of reduction products were defined as

$$\gamma = \frac{M_{Fe}}{T_{Fe}} \times 100\% \quad (2)$$

3 Results and discussion

3.1 Direct reduction in microwave field

3.1.1 Phase transitions during reduction

The XRD results of Sample 4 held for various time at 1073 K in microwave field are depicted in Fig. 3. The phases of graphite, metallic Fe and Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ could be observed at this temperature, and Na₂TiO₃ phase emerged at 0 min (Fig. 3(a)). The peak intensities of C and Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ phases gradually decreased, while those of metallic Fe and Na₂TiO₃ increased, as the reaction continued. It can be inferred that Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ is an intermediate phase in the process. The peaks of Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ phase almost disappeared when the sample was held for 20 min, which was chosen as an optimized holding time.

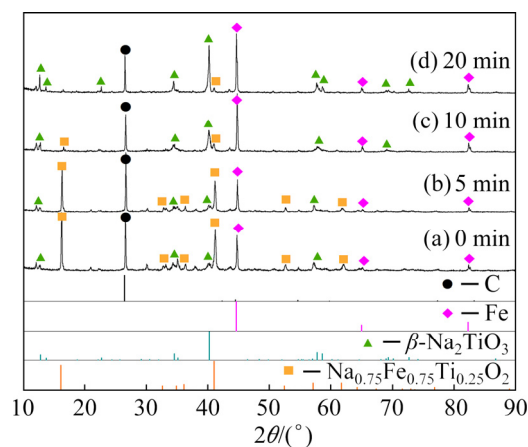


Fig. 3 XRD patterns of reduction products held for different time

The XRD patterns of Sample 4 held for 20 min at different temperatures (1023–1173 K) in microwave field are depicted in Fig. 4, where the main products were metallic Fe and Na₂TiO₃. As an intermediate product, the peak intensity of Na_{0.75}Fe_{0.75}Ti_{0.25}O₂ phase decreased gradually with the increase of heating temperature. Na₂TiO₃ was the target product and its peak intensity was enhanced with the increase of reduction temperature from 1023 to 1123 K. However, Na₂TiO₃ was reduced to Na_{0.99}TiO₂ when the heating temperature

was increased to 1173 K, which can be obtained from the comparison between Figs. 4(c) and (d). As a result, 1123 K was selected as the optimized heating temperature in microwave field.

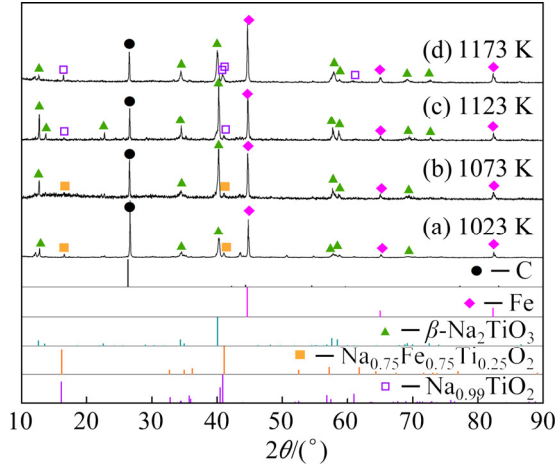


Fig. 4 XRD patterns of reduction products heated at different temperatures

The influence of Na_2CO_3 addition on the final products was also investigated through the XRD results. As illustrated in Fig. 5(a), ilmenite was reduced to metallic Fe, rutile and TiO when no Na_2CO_3 was added, indicating that the reduction was incomplete. In order to eliminate the influence of insufficient C, excessive C was added to the Sample 2 (Fig. 5(b)) for comparison. The phases of the reduction products in Fig. 5(b) didn't change much compared with those in Fig. 5(a), which means the amount of C in Sample 1 is sufficient

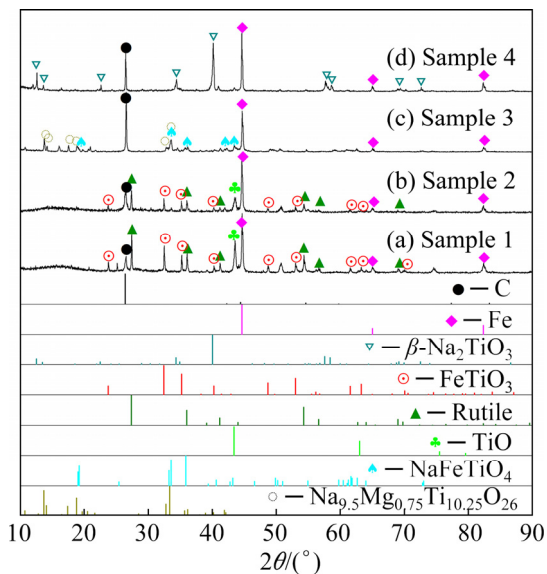


Fig. 5 XRD patterns of reduction products with different Na_2CO_3 additions

for the reduction reaction. As depicted in Fig. 5(c), ilmenite was reduced to metallic Fe, NaFeTiO_4 and $\text{Na}_{0.5}\text{Mg}_{0.75}\text{Ti}_{10.25}\text{O}_{26}$ with the addition of $0.5\text{Na}_2\text{CO}_3$ (0.5 reaction equivalent, Sample 3). In other words, the addition of Na_2CO_3 changed the reaction pathway, which makes the ilmenite reduced more easily. However, the reaction was incomplete with the addition of $0.5\text{Na}_2\text{CO}_3$ for the reduction products containing NaFeTiO_4 phase, which can be reduced to metallic Fe. After adding sufficient Na_2CO_3 in Sample 4, ilmenite was totally reduced to metallic Fe and Na_2TiO_3 (Fig. 5(d)).

To confirm the effect of microwave heating, Sample 4 was reduced at 1073 K for 20 min by conventional electric heating for comparison. The XRD patterns of the reduction products are illustrated in Fig. 6, where XRD patterns of ilmenite and raw materials are also plotted. It is easy to find that Sample 4 was reduced to the intermediate phase of $\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_2$ by electric heating (Fig. 6(c)), while it was reduced to the target products (Fe and Na_2TiO_3) by microwave heating (Fig. 6(d)). By combining the XRD results in Figs. 6(c) and (d), it can be concluded that microwave heating benefits for the reaction in the same condition of heating.

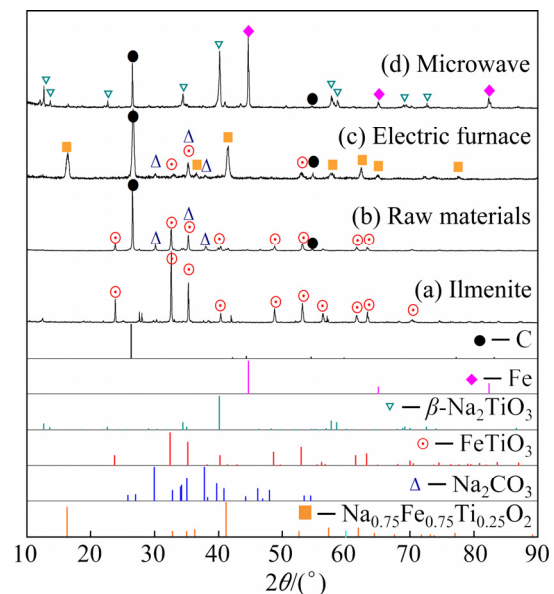


Fig. 6 Comparison of XRD patterns of reduction products by microwave and electric heating

3.1.2 Metallization ratios of reduction products

The metallization ratios of the reduction products heated at different temperatures for 20 min

in microwave field are depicted Fig. 7. The metallization ratios increased first and then declined with the increase of reduction temperature. The reducibility of graphite is enhanced with the increase of reduction temperature [10], which may be the main contribution to the increased metallization ratios. When the heating temperature was increased to 1173 K, the metallization ratio decreased, which can be attributed to the formation of $\text{Na}_{0.99}\text{TiO}_2$. As shown in Fig. 4(d), Na_2TiO_3 was reduced to $\text{Na}_{0.99}\text{TiO}_2$ when the heating temperature was increased to 1173 K. The formation of $\text{Na}_{0.99}\text{TiO}_2$ phase may change the porosity of reduction system and harden the reduction products. In the process of titrimetric analyses, the metallic Fe cannot react completely due to the densification of the reduction products.

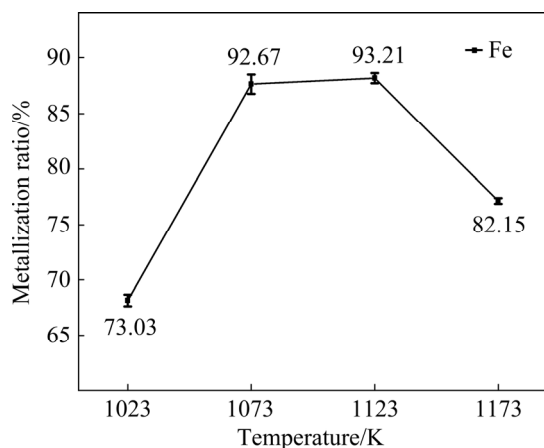


Fig. 7 Variation of metallization ratios with temperature

In order to confirm this assumption, the filtered residue of reduction products after testing the metallization ratio was examined by XRD. As shown in Fig. 8, Fe was observed in the residue after titrimetric analyses, which can support the assumption above.

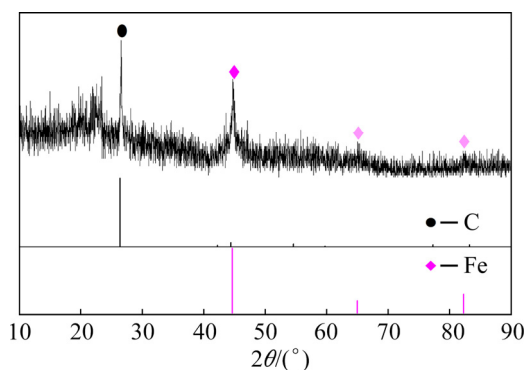


Fig. 8 XRD patterns of filtered residue after titrimetric analyses

3.1.3 Morphology of reduction products

The reduction products were analyzed by SEM and EDS to gain insight into the reduction mechanism. The SEM images of Sample 4 held for 20 min at 1073, 1123 and 1173 K are illustrated in Fig. 9. The main reduction products were metallic Fe and Na_2TiO_3 with many cracks and holes, which may be caused by the release of CO and/or CO_2 at the reduction stage. The tendency that the structure of Na_2TiO_3 transformed from sheet to block with the increase of reduction temperature could also be found.

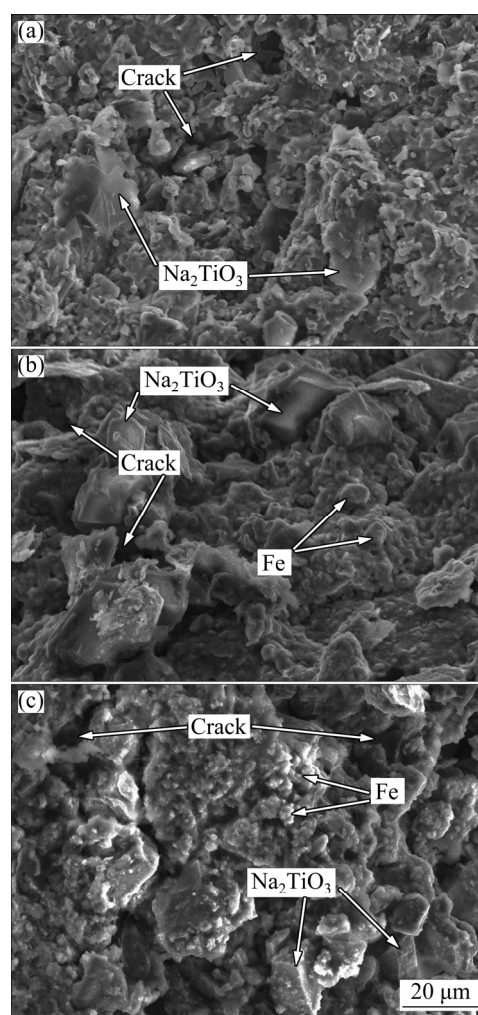


Fig. 9 SEM images of reduction products of Sample 4: (a) 1073 K; (b) 1123 K; (c) 1173 K

As shown in Fig. 10, the distributions of Fe, Ti, Na and O were obtained at the selected areas of the products reduced at 1073, 1123 and 1173 K, respectively. Ti and Fe were gradually separated in the reduction products with the increase of reduction temperature, and the size of the metallic Fe tended to grow larger. Large size of metallic Fe

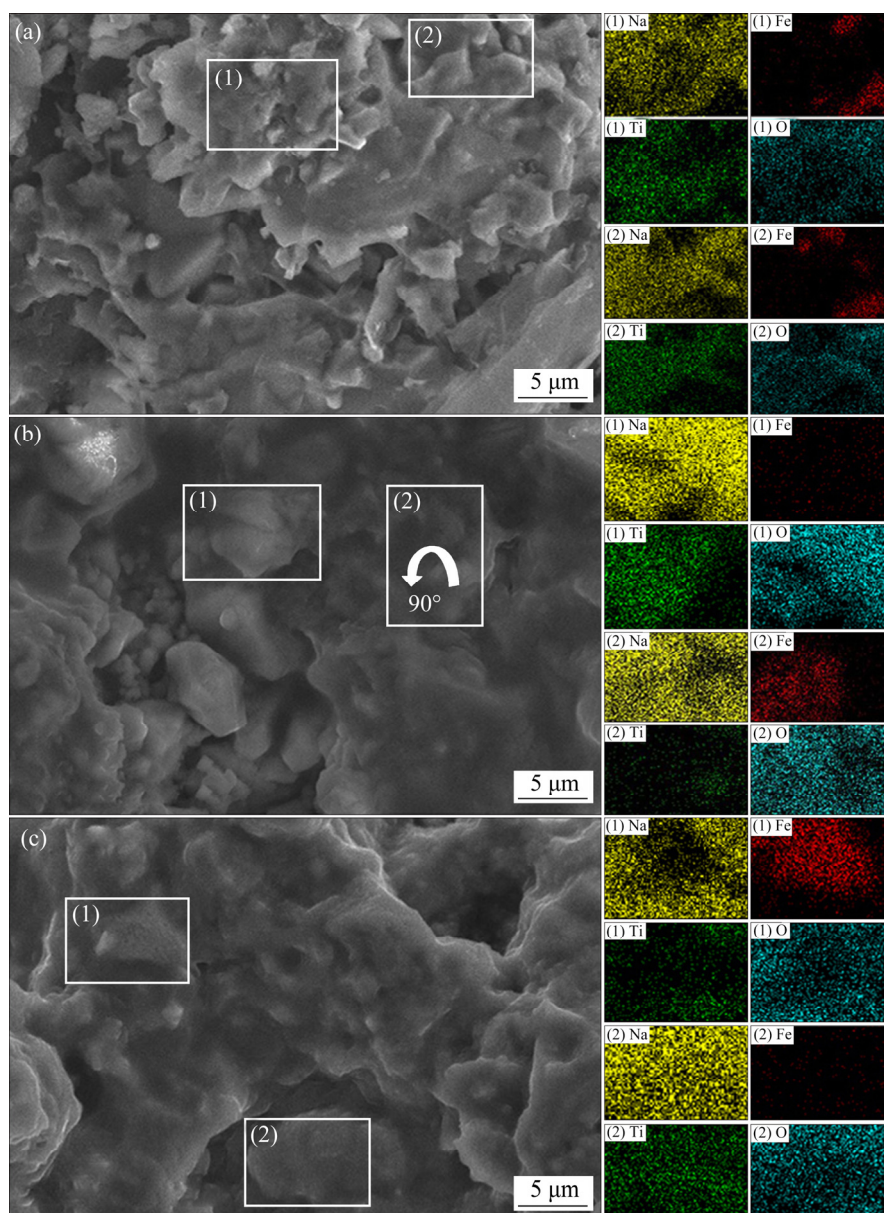


Fig. 10 SEM images and EDS results of reduction products of Sample 4: (a) 1073 K; (b) 1123 K; (c) 1173 K

is good for improving the efficiency of magnetic separation, which can be set as one of the factors for optimizing the heating temperature.

3.2 Preparation of Ti-rich materials

3.2.1 Magnetic separation

As shown in Fig. 11, the reduction products were processed with the steps of water leaching, ball-milling in CO_2 atmosphere and magnetic separation to produce Ti-rich and Fe-rich materials, which were dried at 373 K for 12 h. The contents of Ti and Fe in Ti-rich and Fe-rich materials obtained from reduction products at different temperatures are illustrated in Fig. 11.

As depicted in Fig. 11(a), the content of Ti

increased, while that of Fe decreased, with the increase of reduction temperature in the Ti-rich materials. Besides, the increasing tendency slowed down in the temperature range of 1123–1173 K. However, the content of Fe increased slowly with the increase of reduction temperature in the Fe-rich materials (Fig. 11(b)), while the content of Ti increased first and then decreased. In the reduction process, the metallic Fe grew and gathered with the increase of reduction temperature. At this time, some Ti-containing species might be covered by metallic Fe at 1123 K, and then be uncovered when the temperature was increased to 1173 K, which may be the reason for the change of Ti content in Fe-rich materials.

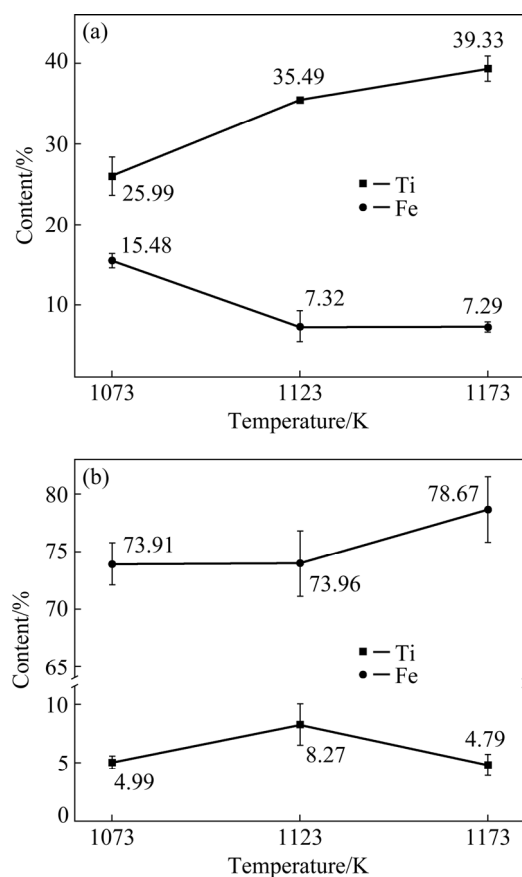


Fig. 11 Content variations of Ti and Fe in separated materials: (a) Ti-rich materials; (b) Fe-rich materials

3.2.2 Final products

It was demonstrated by experiment that the caking problems of the sample adhering to the BN crucible would occur at lower temperature (1123 and 1073 K), while that would not occur at higher temperature (1173 K). At 1173 K, Na_2CO_3 was melted, and the sample would adhere to the crucible, which may result in the corrosion of furnace. Considering the results of metallization ratio, magnetic separation and caking problems, 1123 K was optimized as a suitable reduction temperature.

The XRD patterns of the Ti-rich and Fe-rich materials are illustrated in Fig. 12, where the main products were TiO_2 and Fe in Ti-rich and Fe-rich materials, respectively.

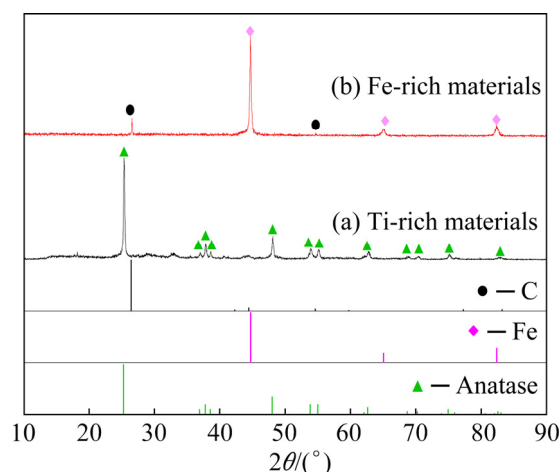


Fig. 12 XRD patterns of final products

The compositions of Ti-rich materials marked with T1, T2 and T3 obtained by the same procedures were analyzed by X-ray fluorescence (XRF) and the results are shown in Table 3.

Supposing that TiO_2 was the only oxide of titanium, then the content of TiO_2 in Ti-rich materials can be calculated according to the following equation:

$$w_{\text{TiO}_2} = w_{\text{Ti}} \cdot \frac{M_{\text{TiO}_2}}{M_{\text{Ti}}} \quad (3)$$

where w_{TiO_2} and w_{Ti} are the mass fractions of TiO_2 and Ti; M_{TiO_2} and M_{Ti} are the molar masses of TiO_2 and Ti. However, the mass fractions of Samples T1, T2 and T3 will be 100.71%, 100.86% and 100.41%, if calculated by Eq. (3). The results ($\geq 100\%$) suggest the existence of other oxides of titanium besides TiO_2 , such as Ti_2O_3 , whose content is too little to be detected by XRD. The real mass fraction of TiO_2 (w'_{TiO_2}) should be calculated by the following equation:

$$w'_{\text{TiO}_2} = \frac{w_{\text{TiO}_2}}{w_{\text{TiO}_2} + w_{\text{Impurities}}} \quad (4)$$

where $w_{\text{Impurities}}$ is mass fraction of impurities, such as CaO, MgO and SiO_2 , which can be obtained through Table 3.

Table 3 Chemical compositions of Ti-rich materials (wt.%)

Sample	Ti	MgO	CaO	MnO	SiO_2	Fe_2O_3	Cr_2O_3	Na_2O	Al_2O_3	Others
T1	60.36	3.40	2.55	1.68	1.12	0.61	0.63	0.62	0.16	0.21
T2	60.45	3.44	1.33	1.37	1.88	0.43	0.86	0.54	0.64	0.19
T3	60.18	3.88	2.62	1.64	1.23	0.61	0.60	0.69	0.16	0.24

According to Eq. (4), the real purity of TiO_2 in Ti-rich materials was 90.16, 90.41 and 89.56 wt.% for Samples T1, T2 and T3, respectively. The average purity of the three samples was 90.04 wt.%, which demonstrates the feasibility of the above process. Fe-rich and Ti-rich materials obtained by this technique can be used as raw materials to produce iron by the electric furnace and to produce TiCl_4 by chlorination process [7], respectively. In addition, Ti-rich materials can also be used to produce TiO_2 in a series of processes. For the preparation of Ti-rich materials, the reduction temperature was prior to be considered in the work. However, other parameters, such as size of metallic Fe, ball-milling time, hydrolysis rate of Na_2TiO_3 and partial pressure of CO_2 , will also influence the efficiency of magnetic separation. It is expected to improve the efficiency of magnetic separation of Ti and Fe by adjusting these parameters to obtain a higher quality of Ti-rich materials.

3.3 Mechanism of reduction in microwave field

The reduction mechanism of the sample in microwave field is presented in Fig. 13.

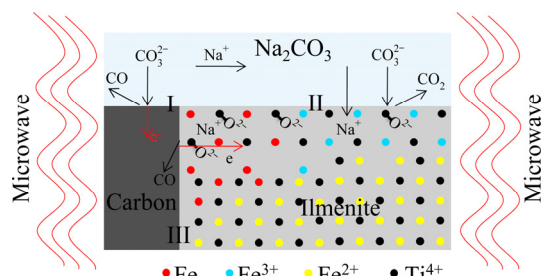
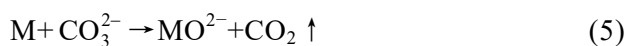
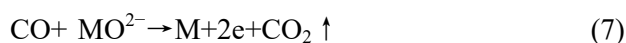


Fig. 13 Schematic diagram of reduction mechanism in microwave field

Reaction occurring at Interface II:



Reactions occurring at Interface III:



where M represents the species containing Ti and O.

As shown in Fig. 13, both graphite and ilmenite can absorb the microwave to improve the

reaction activities. At Interface II, CO_3^{2-} could combine with ilmenite and generate CO_2 and Na^+ , and Na^+ would diffuse into the matrix of ilmenite. At Interface III, on one hand, C or CO lost 2e when combined with MO^{2-} with the absorbing of microwave; on the other hand, Fe^{2+} obtained 2e and lost the bonds with oxygen and titanium, which altered the structure of the matrix of ilmenite. The alterations promoted the transferring capability of electrons in ilmenite, which intensified the reduction of ilmenite. Another possible mechanism is a direct route where CO_3^{2-} combined with graphite at the Interface I [32,33], with the reaction below, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ was reduced to Fe in the reactions occurring at Interface III.



However, under electrical heating, the reduction product was only $\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_2$, without the formation of Fe (Fig. 6(c)), indicating that no reactions occurred at Interface III (Fig. 13). The differences in reaction activities of graphite and ilmenite under microwave heating and electrical heating might lead to those two reaction mechanisms.

4 Conclusions

(1) The optimized heating temperature was 1123 K in terms of metallization ratios, magnetic separation and caking property of the reduction products.

(2) With the addition of Na_2CO_3 , the reduction temperature and time were significantly decreased.

(3) The improved reaction activities of graphite and ilmenite under microwave heating might contribute to the direct carbon-thermic reduction of ilmenite concentrates with Na_2CO_3 addition.

(4) After microwave heating in the temperature range of 1073–1123 K for 20 min, the main products of the sample were Na_2TiO_3 and metallic Fe with the metallization ratios being as high as 92.67%–93.21%.

(5) The purity of TiO_2 in Ti-rich materials was 90.04 wt.%, which can be used as raw materials to produce TiCl_4 or TiO_2 . It is expected to develop a clean and efficient route for the utilization of ilmenite by adding high dosage of Na_2CO_3 in microwave field.

Acknowledgments

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微波场下基于 Na_2CO_3 大剂量添加直接碳热法还原钛铁矿

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摘要: 提出一种基于直接碳热还原和微波加热的钛铁矿绿色高效利用新工艺。通过添加高剂量的 Na_2CO_3 加速还原反应的进行, 并且 Na_2CO_3 可以循环利用。反应原料(钛铁矿+石墨+ Na_2CO_3)在微波场下加热至 1073~1123 K, 保温 20 min 后, 主要还原产物为 Na_2TiO_3 和金属铁, 其中铁的金属化率可以达到 92.67%~93.21%。还原产物依次经过水洗、 CO_2 气氛中球磨和磁选分离, 最终可以得到富铁料和富钛料。其中富钛料中 TiO_2 含量可以达到 90.04% (质量分数), 并可后续用于生产 TiCl_4 或 TiO_2 。基于金属化率、磁选分离效率和产物结瘤特性等参数, 优化得到的还原温度为 1123 K。此外, 还提出添加 Na_2CO_3 后的钛铁矿在微波场下的还原机理。

关键词: 钛铁精矿; 微波; Na_2CO_3 ; 碳热还原

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