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Effects of Temperature on Fe and Ti in Carbothermic Reduction of Vanadium Titanomagnetite with adding MgO

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Abstract: Effects of temperature on Fe and Ti in carbothermic reduction of vanadium titanomagnetite (VTM) concentrate with adding MgO at 1100~1500°C were investigated. It was found that most of Fe in the VTM concentrate existed in the form of magnetite and a small amount existed as ilmenite; Ti in the VTM concentrate was mainly present in the form of ilmenite. The temperature had significant effects on Fe and Ti: increasing temperature was beneficial to decrease the Fe content in the magnesium titanate mixture, and the Fe content could decrease to 5.47% at 1500°C. Thermodynamic analysis showed that FeTiO₃ and MgO preferentially reacted to form Mg₂TiO₄, followed by MgTiO₃ and MgTi₂O₅ when the temperature increased from 1100°C to 1500°C. Results of X-ray diffraction and scanning electron microscopy-energy dispersive spectroscopy analyzes showed that an intermediate product of MgFe₂O₄ would formed at 1300~1400°C in the actual experiment. This caused the Fe content in the magnesium titanate mixture to increase from 21.32% to 22.85% when the temperature increased from 1200°C to 1400°C. In addition, the size of magnesium titanate particles could increase from a few microns to approximately 100 μm when the temperature increased from 1100°C to 1500°C, which was conducive to realize the separation of metallic iron and magnesium titanate.

Keywords: VTM concentrate, temperature, carbothermic reduction, Fe, magnesium titanate

1. Introduction

Vanadium titanomagnetite (VTM), which contains many useful elements such as Fe, Ti, and V, is an associated and coexisting mineral, which has an high comprehensive utilization value (Pan et al., 2017). The deposit of VTM in Panxi, Sichuan Province, China, which is an important source of iron and titanium (Xue et al., 2017; Mao et al., 2013), accounts for approximately 83% of the total deposit in the country. However, because the VTM in Panxi has a high iron and low titanium content, the conventional grinding process results in approximately 53% of the titanium to enter into the iron concentrate, and blast furnace (BF) slag containing 20%~25% of titanium would be formed after BF ironmaking (Xue et al., 2017). Numerous studies focused on the process of "acid, alkali, high-temperature carbonization and low-temperature chlorination" to recycle titanium resources (Zhang et al., 2015), but the utilization of titanium resources in Panxi is still low.

Compared to the BF process, the non-blast-furnace (NBF) technology has been significantly progressed. Because of its advantage in the treatment of complex minerals, a new approach for the comprehensive utilization of VTM has been developed (Neal et al., 2003; Sun et al., 2015; Kopfle et al., 2008). The carbothermic reduction process, with advantages of a relatively short process, simple operation, and low energy consumption, has become one of important NBF processes for ironmaking and titanium recycling (Samanta et al., 2013; Yu et al., 2015). Sun et al. (Sun et al., 2015) investigated the characteristics of carbothermic reduction of VTM based on thermodynamics. Chen et al. (Chen et al., 2014) analyzed the metalizing reduction and magnetic separation of VTM in Panxi based on hot briquetting. It can be known from related studies (Geng et al., 2015; Chen et al., 2017) that most of Fe was reduced to metallic iron, whereas Ti was still present in the form of oxides after carbothermic

reduction. With magnetic separation, direct reduced iron with an Fe grade of approximately 90 wt% (Gao et al., 2016) and titanium slags with Ti content of approximately 30 wt %~40 wt % (Jiang et al., 2016; Gao et al., 2013) can be obtained. This content of Ti is much higher than that of titanium slag produced by BF progress, however, this titanium slag is still not a qualified raw material for the production of titanium dioxide because of its high impurity (Yu et al., 2017; Zheng et al., 2016). Therefore, it is still difficult to achieve an efficient use of titanium resources by the current direct reduction process.

Magnesium titanate, with an ilmenite structure, is one of key materials for the manufacture of microwave components such as resonators, filters, oscillators, wave guides and antennas. It has gained increasing attention with the rapid progress in mobile communications, intelligent transport systems and wireless applications because of its good dielectric properties (Reaney and Iddles, 2015. Isobe and Unde, 2004; Ohsato, 2013). There are a number of methods to synthesize magnesium titanate ceramics, e.g., solid-state reaction (Zhou et al., 2016), sol-gel (Surendran et al., 2008; Li et al., 2012), high-energy ball milling (Cheng et al., 2015), and chemical-reactive precipitation methods (Parthasarathy and Manorama, 2007). The solid state reaction, using industrial pure TiO₂ and MgO as raw materials, is the most application because of its high yield and simple process. However, the preparation process of its raw materials, such as industrial pure TiO₂, which could be obtained after smelting, calcining, acid leaching, etc. is complicated and costly. Therefore, it is necessary to find new methods to synthesize magnesium titanate.

The research group of author (Chen et al., 2017) previously found that mixing VTM concentrate with 12wt% MgO can reduce Fe to metallic iron and transform Ti to magnesium titanate through the process of carbothermic reduction at 1200°C. This provided a new possibility for realizing the separation of Ti and Fe effectively, and simplified the synthesis process of magnesium titanate compared with current synthesis methods. However, the purity of magnesium titanate is low because of the presence of Fe, thus the author believes that it is necessary to conduct further studies on the process of carbothermic reduction of VTM concentrate with adding MgO.

Therefore, the temperature of the carbothermic reduction of VTM concentrate with adding MgO was increased from 1100°C to 1500°C, and the effect of temperature on Ti and Fe were investigated in this study.

2. Experimental

2.1. Materials

2.1.1 Compositions of chemical and mineral

The VTM concentrate used in this study was obtained from Panxi, Sichuan Province, China. Chemical analysis results are shown in Table 1, in which TFe and TiO₂ content are 53.15wt% and 11.60wt%, respectively.

Table 1. Chemical compositions of the VTM concentrate (wt%)

Total Fe	TiO ₂	CaO	MgO	Al ₂ O ₃	SiO ₂	V ₂ O ₅	MnO
53.15	11.60	1.11	3.33	3.78	3.64	0.55	0.40

Figure 1 shows the X-ray diffraction (XRD, Rigaku D/Max 2500, Japan) pattern of VTM concentrate, where Fe exists mainly in the form of magnetite (Fe₃O₄), Ti is mainly present in the form of ilmenite (FeTiO₃), and the impurity element Al exists mainly in the form of chlorite ((Mg, Fe)₆(Si, Al)₄O₁₀(OH)₈).

The additive was analytically pure MgO, which was sourced from Sinopharm Chemical Reagent Co Ltd, China.

The reductant was bituminous coal with a particle size of less than 1 mm, in which the fixed carbon was 56.66wt%, ash was 6.55wt%, volatile matter was 29.54wt%, and moisture was 7.25wt%.

2.1.2 Microstructure analysis

In order to determine the distribution of Fe and Ti, VTM concentrate was analyzed by scanning electron microscopy (CAMBRIDGES-360, VO18, Carl Zeiss, Germany).

Figure 2a shows that magnetite (point 1) in VTM concentrate is distributed mainly in the shape of a block with a low monomer liberation degree and a particle size from 50µm to 100µm. Chlorites (point 3) are mainly in block shapes, some of them are monomeric liberations with particle size from 20 µm to 100 µm. Other chlorites are cemented together with magnetite in the form of intergrowth with small particle size.

To further analyze the microstructure of individual magnetite particles, frames 1 and 2 in Figure 2 were further enlarged, and the results are shown in Figure 2b and 2c.

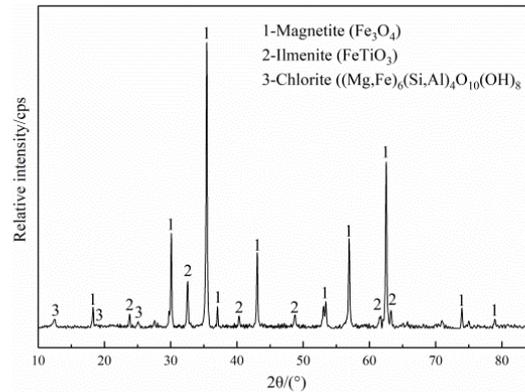


Fig. 1. XRD patterns of VTM concentrate

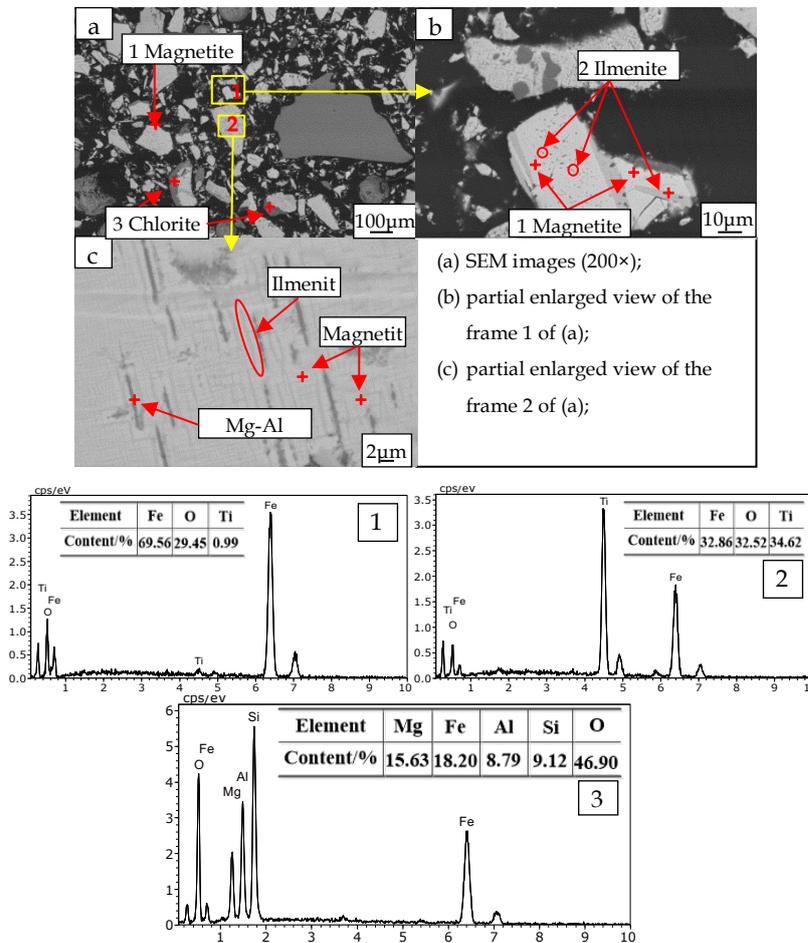


Fig. 2. SEM images of VTM concentrate

Figure 2b and 2c show that magnetite particles in the VTM concentrate are not pure, and many ilmenite particles are existing. Some of ilmenite are encapsulated in magnetite in shapes of fine granular and net with small particle size, and they are associated closely with each other.

Therefore, Fe of VTM concentrate is mainly present in the form of magnetite with large particle sizes; and Ti of VTM concentrate is mainly present in the form of ilmenite with small particle sizes. Furthermore ilmenite is encapsulated in magnetite particle in shapes of fine granular and net, and it is difficult to separate them.

2.2. Experimental procedure

Before the roasting experiments, 150g of VTM concentrate was mixed with 18g of MgO by rod grinding, and 12wt% of water was added to produce pellets with diameters of 8~10mm, these pellets were naturally dried at room temperature for 12h to obtain green pellets. Then, the reduction experiments were performed in a muffle furnace with the following procedure. First, 3 green pellets together with 19.2g of bituminous coal were placed in graphite crucibles (50 mm in diameter and 70 mm in height) with lid. The green pellets were completely embedded in the bituminous coal, and the bituminous coal dosages were determined according to previous test results and remained unchanged at different temperatures to ensure a sufficient reduction atmosphere. Then, the crucibles were placed inside the furnace and maintained for 180min when the temperature reached the designated value. After heating, when the furnace temperature was reduced to 60°C, the crucibles were taken out from the furnace and cooled to room temperature under atmosphere air to obtain roast pellets.

After cooling, a roast pellet was cut along the center line; half of it was treated by grinding to 80wt% -0.074mm to analyze the mineral composition changes by XRD (Rigaku D/Max 2500, Japan). The other half was used as an electron microscope sample to analyze the microstructural changes and the distribution of Ti and Fe by scanning electron microscopy-energy spectroscopy (CAMBRIDGES-360, VO18, Carl Zeiss, Germany).

Then, the roast pellets were crushed to -1mm, and treated by grinding-magnetic separation, in which the grinding time was 20 min and the magnetic field intensity was 2100Gs. The magnetic materials obtained from magnetic separation were named direct reduction iron (DRI), and the non-magnetic materials were named magnesium titanate mixture. The test flow sheet and crucible charging method are shown in Figure 3.

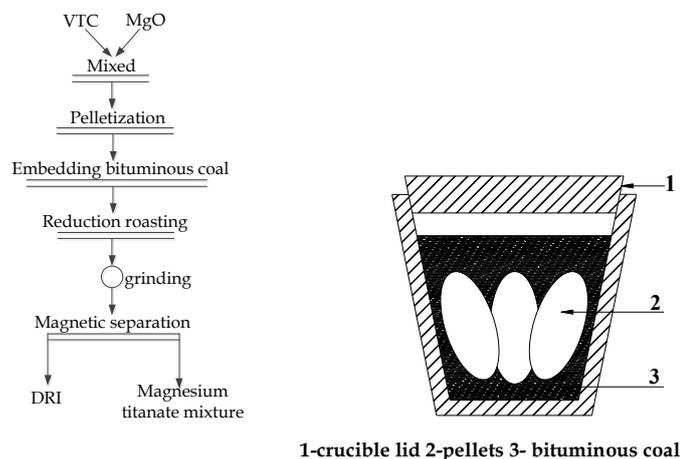


Fig. 3. Test flow sheet and crucible charging method

3. Results and discussion

3.1. Effects of temperature on Fe and Ti

3.1.1 Effects of temperature on the content of Fe

In order to find out the effect of temperature on the content of Fe in the magnesium titanate mixture, magnetic separation was conducted on roast pellets at 1100~1500°C, and different magnesium titanate mixtures were analyzed by chemical titration. The result is shown in Figure 4.

Figure 4 shows that the content of Fe in the magnesium titanate mixture is significantly influenced by temperature. The content of Fe in the magnesium titanate mixture decreases first, increases slightly and then decreases significantly. At 1100°C, the content of Fe in the magnesium titanate mixture is 26.85%; and it decreases to 21.32% when the temperature increased to 1200°C. This indicates that increasing temperature can promote the reduction of iron-containing minerals. The content of Fe in the magnesium titanate mixture increases from 21.32% to 22.85% when the temperature increased from 1200°C to 1400°C; the reason for this is elucidated by a combination of XRD and SEM-EDS analyses. Then, the content of Fe in magnesium titanate concentrate rapidly decreases to 5.47% when the temperature increased to 1500°C, indicated that increasing temperature can significantly decrease the Fe content in the magnesium titanate mixture.

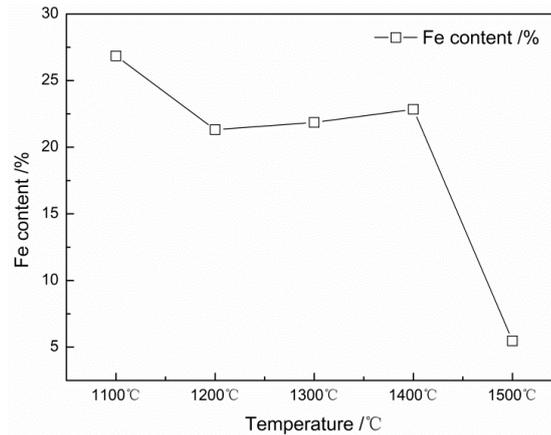
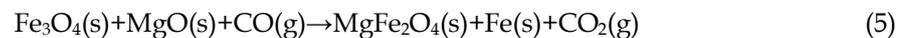
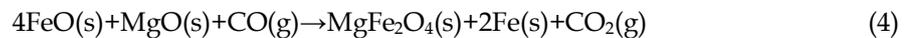
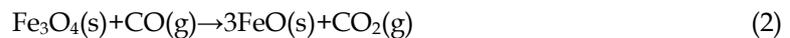
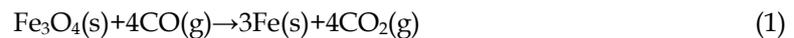


Fig. 4. Effect of reduction temperature on Fe content of magnesium titanate mixture

3.1.2 Effects of temperature on the transformation of Fe

It can be known from the above analysis that temperature has an important influence on the content of Fe in the magnesium titanate mixture. Thus it is necessary to determine effects of temperature on the transformation of Fe during the process of carbothermic reduction of VTM concentrate with adding MgO. According to the result of the material analysis, Fe in the VTM concentrate was mainly present in the form of magnetite, therefore a thermodynamic analysis of the magnetite reduction was conducted. Reactions that might occur in the reduction system are as follows, in which equations (1) to (3) are reactions in the reduction system without adding MgO, whereas equations (4) and (5) are reactions might occur with adding MgO.



According to the reaction equation of the thermodynamic software, HSC, the standard Gibbs free energy ($\Delta_r G_m^\theta$) values of reaction equations (1) to (5) with temperature (T) were calculated and shown in Figure 5

As shown in figure 5, the $\Delta_r G_m^\theta$ of reaction equation (1) is smaller than that of reaction equations (2) and (3) when the temperature is less than 600°C, the $\Delta_r G_m^\theta$ of reaction equation (2) is obviously decreased when the temperature is higher than 600°C, which indicates that the transformation of Fe could be expressed as $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ without adding MgO. Furthermore, it can be observed from Figure 5 that the $\Delta_r G_m^\theta$ of reaction equation (5) is greater than zero at 400°C to 1500°C, which indicates that MgO can not react with Fe_3O_4 in theory. However the $\Delta_r G_m^\theta$ of reaction equation (4) is less than zero in a certain temperature range, which indicates that the unreduced FeO in the reduction system might react with MgO to form MgFe_2O_4 through reaction equation (4). This phenomenon would be explained by a combination of XRD and SEM-EDS analyses.

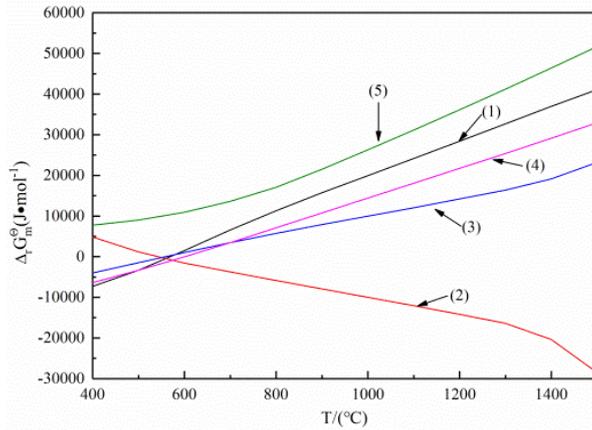
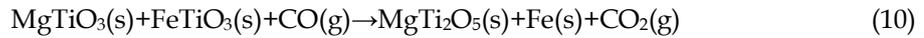
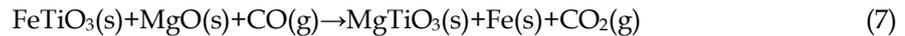
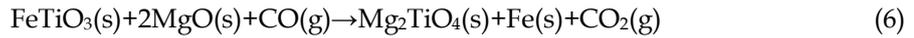


Fig. 5. The relationship between $\Delta_r G_m^\ominus$ and T of reaction equations (1) to (5)

3.1.3 Effects of temperature on the transformation of Ti

It can be known from the material analysis that Ti in the VTM concentrate existed mainly in the form of ilmenite, therefore to find out effects of temperature on the transformation of Ti during the process of carbothermic reduction of VTM concentrate with adding MgO, the thermodynamic analysis of ilmenite reduction was conducted. Reactions that containing ilmenite might occur in the reduction system are as follows:



According to the reaction equation of HSC, the standard Gibbs free energy ($\Delta_r G_m^\ominus$) values of reaction equations (6) to (10) with temperature (T) were calculated and shown in Figure 6.

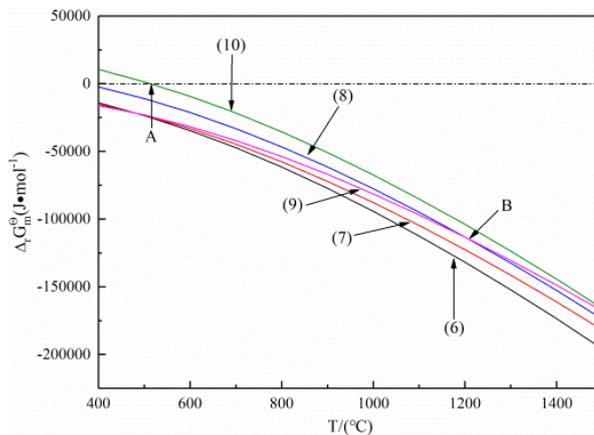


Fig. 6. The relationship between $\Delta_r G_m^\ominus$ and T of reaction equations (6) to (10)

Figure 6 shows that reaction equations (6) to (9) can be carried out spontaneously because their $\Delta_r G_m^\ominus$ values are less than zero in the temperature range of 400~1500°C. Point A indicates that reaction equation (10) cannot proceed spontaneously before 500°C because the $\Delta_r G_m^\ominus$ of reaction equation (10) is greater than zero at this temperature, however, reaction equation (10) can be carried out spontaneously when the temperature is higher than 500°C. Point B is the intersection of reaction equations (8) and (9), the temperature of which is approximately 1250°C. The $\Delta_r G_m^\ominus$ of reaction equation (9) is smaller than that of reaction equation (8) when the temperature is less than 1250°C, which indicates that reaction equation (9) is easier to occur than reaction equation (8) in theory. That

is, before 1250°C, the formation of MgTiO_3 is easier than that of MgTi_2O_5 ; otherwise the reaction to form MgTi_2O_5 is easier in the reduction system. Moreover, the Mg_2TiO_4 formed in the reduction system is unstable, and it would preferentially transform into MgTiO_3 and then gradually transform into MgTi_2O_5 through reaction equation (10) with increasing temperature.

Comparing the $\Delta_r G_m^\theta$ of reaction equations (6) to (10) at various temperatures, it can be found that the $\Delta_r G_m^\theta$ of reaction equation (6) is the smallest, followed by reaction equation (7), (9) or (8), while the $\Delta_r G_m^\theta$ of reaction equation (10) is the largest. This phenomenon indicates that Mg_2TiO_4 is preferentially formed, followed by MgTiO_3 and MgTi_2O_5 during the reduction process of ilmenite with MgO . Therefore, theoretically, with increasing temperature, the existence of Ti can be expressed as $\text{FeTiO}_3 \rightarrow \text{Mg}_2\text{TiO}_4 \rightarrow \text{MgTiO}_3 \rightarrow \text{MgTi}_2\text{O}_5$.

3.2. Results of XRD and SEM-EDS analyses

The above analysis results show that the reduction temperature has significant effects on the content of Fe and existence of Ti. To explain the effect of temperature on Fe and Ti, XRD and SEM-EDS analyses were conducted.

3.2.1 Results of XRD analysis

First, XRD analysis was conducted on different roast pellets at 1100~1500°C and the result is shown in Figure 7.

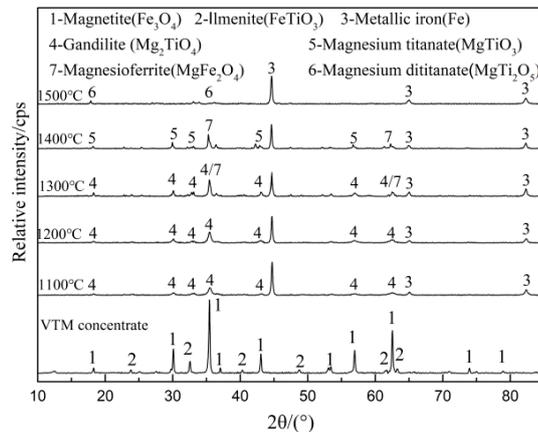
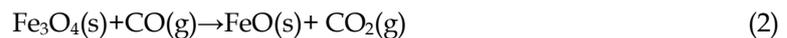
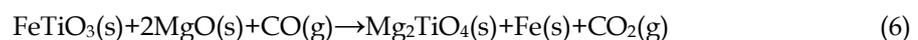


Fig. 7. XRD patterns of roast pellets over a range of temperatures

Figure 7 shows that the temperature has a significance effect on the phase composition and transformation. Fe of VTM concentrate exists mainly in the form of magnetite (1), while Ti exists mainly in the form of ilmenite (2). The XRD pattern at 1100°C shows that Fe and Ti of reduction product exist mainly in the form of metallic iron (3) and Mg_2TiO_4 (4), respectively. This indicates that magnetite (1) is predominantly reduced to metallic iron during roasting. Related studies (Liu et al., 2016; Wang et al., 2016; Yu et al., 2017;) showed that magnetite (1) can be reduced to metallic iron in carbothermic reduction of VTM concentrate with reaction equations (1) and (2).



Similarly, the transformation of ilmenite (2) indicates that Mg_2TiO_4 (5) is formed by the reactions of FeTiO_3 and the added MgO via reaction equations (6) in the reduction system, and this result is consistent with that of the thermodynamic analysis.

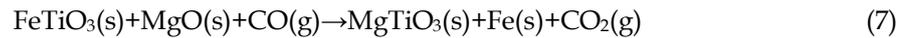


Peaks of metallic iron (3) and Mg_2TiO_4 (4) that existed in the reduction products have increased significantly when the reduction temperature is raised to 1200°C, which indicates that the reduction of metallic iron and formation of Mg_2TiO_4 are promoted with increasing reduction temperature. In other words, an increasing reduction temperature can effectively decrease the content of Fe in the magnesium titanate mixture, therefore the content of Fe in the magnesium titanate mixture decreases

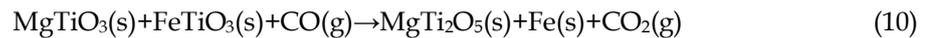
significantly with the reduction temperature increasing from 1100°C to 1200°C (as shown in Figure 4).

It can be observed from the XRD pattern at 1300°C that peaks of metallic iron (3) decrease and those of MgFe_2O_4 (7) appear with increasing reduction temperature. A related study (Shen et al., 2006) showed that magnesium ferrite forms when an iron concentrate powder is mixed with a light-burnt magnesia powder, and its content would increase rapidly with temperature increasing from 1500 K to 1700 K (1227°C~1427°C). This indicates that intermediate product of magnesium ferrite is formed by consuming MgO in the reduction system; this phenomenon was consistent with that of thermodynamic analysis.

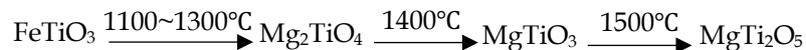
Peaks of MgFe_2O_4 (7) increase continually when the reduction temperature is raised to 1400°C, indicating that increasing temperature can promote the formation of MgFe_2O_4 (7); thus the content of Fe in the magnesium titanate mixture increases with the temperature increasing from 1200°C to 1400°C. Meanwhile the phases of Mg_2TiO_4 (4) are replaced by MgTiO_3 (5), which indicates that increasing temperature is beneficial in forming MgTiO_3 (5) by reaction equations (7) and (9).



Peaks of MgTi_2O_5 (6) appear and those of MgFe_2O_4 (7) disappear in the reduction products with the temperature increasing from 1400°C to 1500°C, which indicates that increasing temperature is beneficial in forming MgTi_2O_5 (6) by reaction equations (8) and (10), as well as in promoting the reduction of MgFe_2O_4 (7); thus, the Fe content decreases significantly with the temperature increasing from 1400°C to 1500°C.



Therefore, the reduction temperature has significant effects on Fe and Ti in the actual experiment. With the reduction temperature increasing from 1100°C to 1500°C, the existence of Ti can be expressed as:



3.2.2 Results of SEM-EDS analysis

To further explain the effect of temperature on Fe and Ti, roast pellets at different temperatures were analyzed by SEM-EDS, and the results are shown in Figure 8.

Figure 8a and 8b show that metallic iron and magnesium titanate particles with sizes from a few microns to approximately 20 μm are formed when the reduction temperature increases from 1200°C to 1300°C, but it is difficult to separate metallic iron and magnesium titanate because there is not obvious boundary between them. It can be observed from figure 6c that the particles sizes of metallic iron and magnesium titanate are increased to approximately 50 μm . Moreover some roast holes appear inside the pellets when the reduction temperature increases to 1400°C, which indicates that increasing temperature can promote the growth of metallic iron and magnesium titanate particles. Figure 6d shows that the metallic iron particles in the roast pellets grow rapidly at 1500°C, and the boundary between metallic iron and magnesium titanate particles becomes increasingly obvious, which is conducive to separate the metallic iron and magnesium titanate through grinding and magnetic separation. Therefore, increasing temperature can decrease the Fe content in the magnesium titanate mixture.

Additionally, the EDS analyses of different minerals at 1200~1500°C were conducted. Energy spectrum points 1, 2 and 4 show that the reduction temperature has significant effects on the Fe content in magnesium titanate and the existence of Ti. The peak of Fe in magnesium titanate increases continuously when the reduction temperature increases from 1200°C to 1400°C, and reaches the maximum at 1400°C. However, the peak of Fe no longer appears when the reduction temperature reaches to 1500°C, which indicates that the Fe content in magnesium titanate drops dramatically at this temperature.

Figures 8b and 8c show that a small amount of slightly dark particles (Figure6c point 3 and Figure6c point 5) with sizes of approximately 10 μm to 40 μm are connected closely with the

magnesium titanate particles. Through EDS analysis and the results of points 3 and 5, it can be found that these slightly dark particles were magnesium ferrite, whose content increases with increasing temperature. Thus, it can be concluded that an intermediate product of magnesium ferrite would form and dissolve in magnesium titanate particles in the process of reducing ilmenite into metallic iron, and its content at different temperatures has an important effect on the intensity of Fe peak in the energy spectrum. This result is consistent with that of XRD analysis.

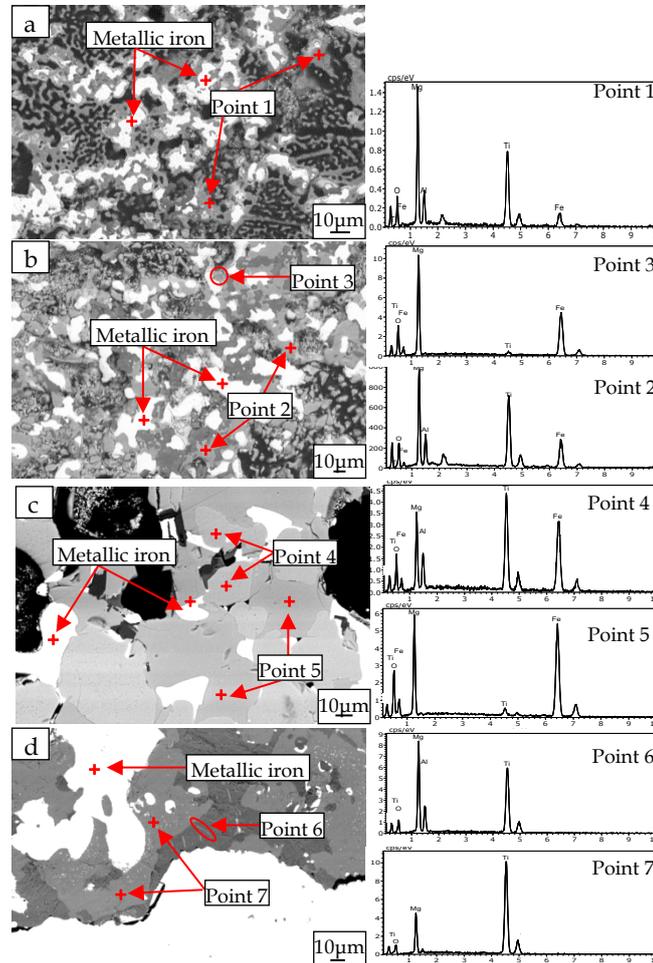


Fig. 8. SEM images and EDS analysis of roast pellets

It can be observed from Figures 8a to 8d that increasing temperature can not only decrease the Fe content in magnesium titanate, but also affect the existence of Ti. At 1200~1300°C, Ti exists in the form of $MgTiO_4$, while the distribution of $MgTiO_3$ increases gradually when the reduction temperature increases to 1400°C. At 1500°C, an increasing amount of $MgTi_2O_5$ appears in roast products, which indicates that Ti content in magnesium titanate increases significantly with the reduction temperature increasing from 1200°C to 1500°C. The above phenomenon is consistent with the result of XRD analysis.

In addition, it can be observed from the energy spectrum of different types of magnesium titanate that the temperature has a minor effect on the content of Al in magnesium titanate. Thus the removal of Al in magnesium titanate will be the focus of the next research work. First, the test of roasting time and coal types will be carried out. Then, the magnesium titanate obtained by magnetic separation under the optimal condition will be leached by acid to reduce the content of impurity.

4. Conclusions

In summary, effects of temperature on Fe and Ti in carbothermic reduction of VTM concentrate with adding MgO were investigated. It was found that the content of Fe in the magnesium titanate mixture first decreased from 26.85% to 21.32% when the temperature increased from 1100°C to 1200°C. Then, it

increased to 22.85% as the temperature increased to 1400°C, and finally decreased to 5.47% when the temperature increased to 1500°C. This indicated that increasing temperature was beneficial to decrease the Fe content in the magnesium titanate mixture. Results of XRD and SEM-EDS analyses showed that an intermediate product of MgFe_2O_4 would form at 1300~1400°C in the actual experiment, which caused the Fe content in the magnesium titanate mixture to increase from 21.32% to 22.85% when the temperature increased from 1200°C to 1400°C. In addition, thermodynamic and XRD analyses showed that the transformation of Ti was greatly affected by the reduction temperature, which could be expressed as:



It could be found from SEM-EDS analysis that the size of magnesium titanate particles could increase from a few microns to approximately 100 μm with the temperature increasing from 1100°C to 1500°C, which was conducive to realize the separation of metallic iron and magnesium titanate.

Acknowledgments

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