Feasibility study on preparation of magnesium titanate in carbonthermic reduction of vanadium titanomagnetite concentrates

Chao Chen, Ti-Chang Sun, Jue Kou, Xiao-Ping Wang, Yong-Qiang Zhao

School of Civil and Resource, University of Science and Technology Beijing, Beijing, 100083 PR China

Corresponding author: suntichang@163.com (Ti-Chang Sun)

Abstract: Effect of temperature and Mg:Ti ratio on phase composition and microstructure of reduced pellets was investigated to verify the feasibility of preparation of magnesium titanate by adding MgO in carbonthermic reduction of the vanadium titanomagnetite concentrates (VTC). Thermodynamic analysis results showed that magnesium titanate is more easily generated than $FeTi_2O_5$ or TiO_2 by the reaction of $FeTiO_3$ and MgO under the reductive atmosphere, which was confirmed by the discovery of magnesium titanate at roast experiment. It was found that the optimum conditions for reduction of VTC pellets were temperature of 1250 °C and Mg:Ti ratio of 2, and the main phases of reduction product were metallic Fe and magnesium titanate (Mg_2TiO_4). However, trace iron impurities in Mg_2TiO_4 particles were found by energy-dispersive spectroscopy (EDS), so further purification is required.

Keywords: Vanadium titanomagnetite, carbonthermic reduction, magnesium titanate, formation mechanism

1. Introduction

Vanadium titanomagnetite is an abundant resource of vanadium, titanium, and iron. This mineral is a massive, special iron-ore deposit with total reserves of more than 40 billion tons in the world (Chen and Chu, 2014). However, comprehensive utilization processes such as blast furnace and converter are applicable to recovery only of iron and vanadium, and titanium mostly remains in the blast furnace slag (Fu et al., 2011; Du et al., 2012; Chen et al., 2011). Thus, a new method of recovering all valuable metal elements is necessary.

Vanadium titanomagnetite typically contains impurities such as CaO and MgO (Liu et al., 2014). In numerous, previous studies on the reduction of vanadium titanomagnetite ore (Chen et al., 2013; Hu et al., 2014; Paunova, 2002; Zhao et al., 2015; Lv et al., 2013; Sun et al., 2015), magnesium is found to combine with titanium and form magnesium–titanium oxide compound. Hu et al. (Hu et al., 2014) studied the reduction behaviour of Panzhihua vanadium titanomagnetite concentrates with coal under argon atmosphere at different temperatures. The formation of Mg_2TiO_4 and $(Fe,Mg)Ti_2O_5$ was observed above 1100°C, and $MgTiO_3$ was formed at 1350°C. On the other hand Zhao et al. (Zhao et al., 2015) investigated the reduction process of vanadium titanomagnetite under the conditions of C:O of 1 and temperature of 1350°C. It was proved that the phase transformation of titanium compounds proceed along the sequence of $FeTiO_3 \rightarrow Fe_5TiO_8 \rightarrow Fe_2TiO_5 \rightarrow Mg_2TiO_4 \rightarrow (Fe,Mg)Ti_2O_5$.

Notably, magnesium titanate is classified as a basic dielectric material, which is widely used in the field of precision electronic ceramics, such as ceramic capacitors (Ovchar et al., 2004). In particular, Mg_2TiO_4 and $MgTiO_3$ exhibit excellent dielectric properties and spectrum reflection characteristics and can act as an ideal functional fillers for coatings (Huang et al., 2005). Magnesium titanate powder is usually prepared by the solid-phase reaction of magnesium oxide (MgO) and titanium dioxide (TiO2) (Sreedhar and Pavaskar, 2002), this process requires high-purity, expensive TiO_2 as a raw material. Under the assumption that MgO addition to the carbonthermic reduction of vanadium titanomagnetite promotes the combination of magnesium and titanium to form magnesium titanate, the recovery of

vanadium, titanium, and iron from vanadium titanomagnetite can be an economically efficient approach.

Therefore, in the current study, MgO as an additive was introduced to the reduction process of vanadium titanomagnetite concentrates (VTC) with coal, and the feasibility of preparation of magnesium titanate was investigated by thermodynamic analysis, X-ray powder diffraction (XRD), and scanning electron microscopy (SEM).

2.   Materials and methods

2.1. Materials

The chemical composition and size distribution of VTC (Chengde, China) were examined and are presented in Table 1 and Table 2. As shown in Table 2, the VTC particles are extremely fine, with a −0.074 mm portion of approximately 88%.

Table 1. Chemical composition of VTC

Component	Total Fe	FeO	Fe_2O_3	MgO	Al_2O_3	SiO_2	TiO_2	V_2O_5	CaO
Content (%, ω)	58.85	30.12	52.02	0.66	3.59	2.03	7.35`	0.75	0.34

Table 2. The size composition of VTC

Size (mm)	-0.045	0045~0.074	+0.074
Content (%)	55.08	32.76	12.16

The coal used in this study was a bituminous coal from Henan China, with the composition given in Table 3. The coal was prepared by crushing in a roll crusher and passing through a 0.5 mm sieve. Analytically pure MgO was added as a raw material.

Table 3. Composition of bituminite

Component	Fixed carbon	Ash	Volatiles	Total sulphur
Content (%, ω)	56.23	11.13	32.62	0.02

X-ray diffraction and SEM scanning analysis of VTC are shown in Fig. 1 and 2. The major mineral compositions are magnetite and ilmenite, which is typically a kind of vanadium titanomagnetite ore.
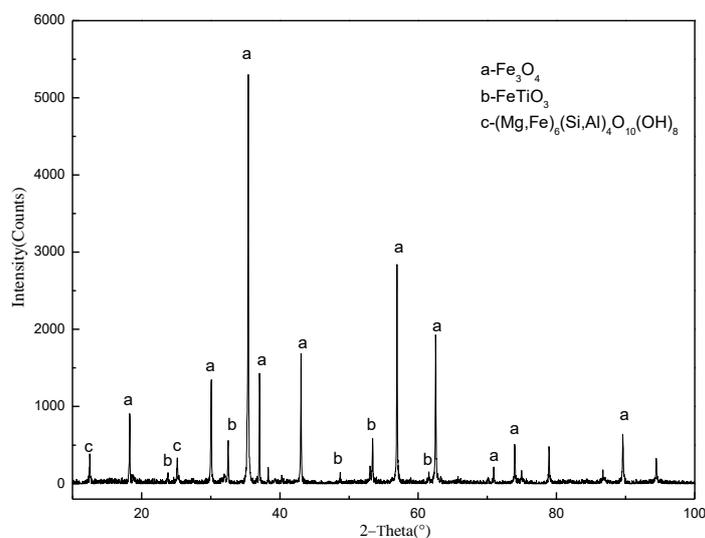
Fig. 1. XRD pattern of VTC
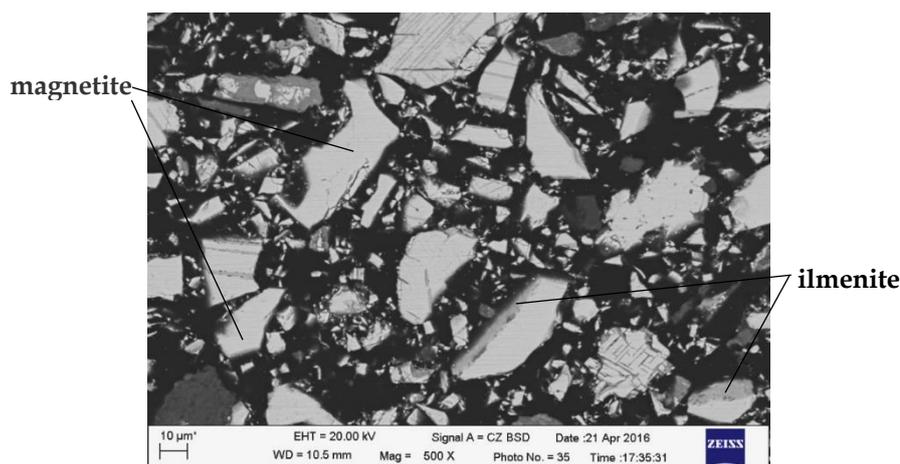
Fig. 2. SEM micrograph of VTC

2.2. Experimental procedures

Compact composition of several different ratios of magnesium to titanium (Mg:Ti) were prepared to test different variables. The Mg:Ti ratio was defined as the mole ratio of magnesium from the VTC and the added MgO to the total titanium content in the VTC. The VTC and added MgO were homogeneously mixed by a high-speed roller mill for 30 s. The different mixtures used during the study are provided in Table 4.

Table 4. Mass percent of constituents of mixture with different Mg:Ti mole ratios

Mg:Ti	1	2	3	4
VTC(%)	96.93	93.73	90.61	87.69
Adding MgO(%)	3.07	6.27	9.39	12.31

The mixtures added with distilled water were shaped into spheroid briquette by using a briquette maker under a pressure of 15 MPa. The briquette was 30 mm in diameter, and the total mass of the sample was approximately 20 g. All briquettes were dried in an oven for 2 h at 110°C prior to the reduction experiments.

A single briquette was used for each experiment. The briquette was placed into a cylindrical Al_2O_3 crucible, and 20 g bituminous coal was added to cover the briquettes fully to ensure complete reduction. Reduction of the VTC briquettes was conducted by heating the compacts under nitrogen in a sealed furnace. The furnace temperature was increased at an average of 10°C/min, and a 60 min holding time was applied when the temperature reached the target temperature.

After the reduction experiments, the briquettes were rapidly removed and quenched. The phase structure and microstructure of reduced briquettes was examined by XRD and SEM, respectively. EDS was used to provide semi-quantitative elemental analyses of different points within the cross-sections of the samples. The metallization of the VTC briquettes (η) can be calculated by Eq (1).

$$\eta = \frac{MFe}{TFe} \times 100\%$$

(1)

where *MFe* is the content of metallic iron, and *TFe* is the content of total iron. *MFe* and *TFe* were determined by chemical titration.

3. Results and discussion

3.1. Thermodynamic analysis of reduction of ilmenite

Previous analyses of the properties of VTC showed that main phase components are magnetite and ilmenite. It was stated that this study focused on the reaction between Ti and Mg, so thermodynamic analysis between MgO and ilmenite was carried out below.

At the beginning of the reduction, given the protection of nitrogen and the lack of other reductant source except for carbon, and in the absence of MgO, ilmenite was the most likely to be reduced by the direct reduction followed reactions (2) and (3). Otherwise, with the presence of MgO, the most possible reduction reaction would be reactions (4), (5), and (6).

$$2FeTiO_{3(s)} + C_{(s)} \rightarrow FeTi_2O_{5(s)} + Fe_{(s)} + CO_{(g)} \tag{2}$$

$$FeTiO_{3(s)} + C_{(s)} \rightarrow Fe_{(s)} + TiO_{2(s)} + CO_{(g)} \tag{3}$$

$$FeTiO_{3(s)} + 2MgO_{(s)} + C_{(s)} \rightarrow Mg_2TiO_{4(s)} + Fe_{(s)} + CO_{(g)} \tag{4}$$

$$FeTiO_{3(s)} + 1/2MgO_{(s)} + C_{(s)} \rightarrow 1/2MgTi_2O_{5(s)} + Fe_{(s)} + CO_{(g)} \tag{5}$$

$$FeTiO_{3(s)} + MgO_{(s)} + C_{(s)} \rightarrow MgTiO_{3(s)} + Fe_{(s)} + CO_{(g)} \tag{6}$$
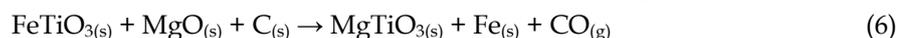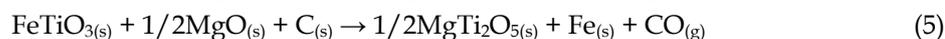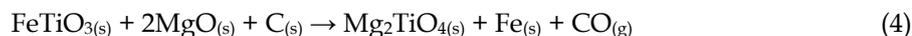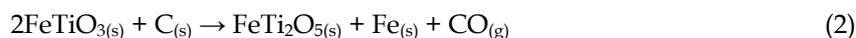
According to reaction module of Factsage (Bale et al., 2008), the standard Gibbs free energy (ΔrG_m^θ) of reactions (2) to (6) was calculated and shown in Fig. 3 as a function of temperature. Evidently, the ΔrG_m^θ of reactions (2) and (3) is higher than the ΔrG_m^θ of reactions (4), (5), and (6) in the total reducing temperature under standard state. In addition, the lowest ΔrG_m^θ observed for reaction (3) was obtained when the temperature exceeded 1310K. This finding indicates that ilmenite is more easily reduced by reactions (4), (5), and (6) in the presence of MgO, and the formation of Mg_2TiO_4 more easily occurs with increasing temperature.
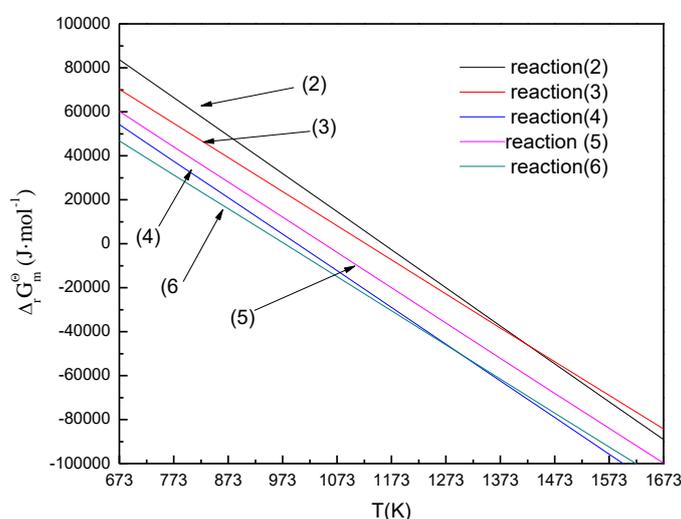
Fig. 3. Standard Gibbs free energy of ilmenite reduced by carbon vs. temperature

As the reduction proceeds, CO content increases and solid–solid reaction is inhibited by a mass transfer and interface reaction, and the dominant reduction reaction is switched to gas–solid reaction. With CO as the reducer, the most plausible reduction reactions of ilmenite are reactions (7) and (8) without MgO. Similarly, reactions (9), (10), and (11) may occur in the presence of MgO. The carbon gasification is a reaction (12).

$$2FeTiO_{3(s)} + CO_{(g)} \rightarrow FeTi_2O_{5(s)} + Fe_{(s)} + CO_{2(g)} \tag{7}$$

$$FeTiO_{3(s)} + CO_{(g)} \rightarrow Fe_{(s)} + TiO_{2(s)} + CO_{2(g)} \tag{8}$$

$$FeTiO_{3(s)} + 2MgO_{(s)} + CO_{(g)} \rightarrow Mg_2TiO_{4(s)} + Fe_{(s)} + CO_{2(g)} \tag{9}$$

$$FeTiO_{3(s)} + 1/2MgO_{(s)} + CO_{(g)} \rightarrow 1/2MgTi_2O_{5(s)} + Fe_{(s)} + CO_{2(g)} \tag{10}$$

$$FeTiO_{3(s)} + MgO_{(s)} + CO_{(g)} \rightarrow MgTiO_{3(s)} + Fe_{(s)} + CO_{2(g)} \tag{11}$$

$$C + CO_{2(g)} \rightarrow 2CO_{(g)} \tag{12}$$
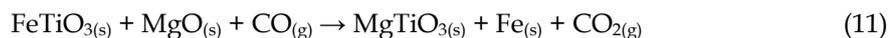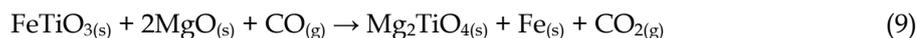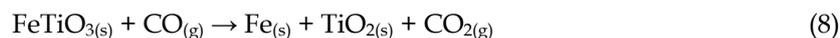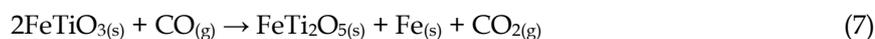
The ΔrG_m^θ of reactions (7) to (11) with temperature is shown in Fig. 4. The standard Gibbs free energy of the reduction reaction of ilmenite by CO is always positive with entire range of reduction temperature, meaning that the equilibrium constants of the reactions (K), that can be obtained from Eq. (13), is extremely small. Therefore, high CO content is necessary to facilitate the reaction.

$$K = \frac{\varphi(CO_2)}{\varphi(CO)} \tag{13}$$

Physicochem. Probl. Miner. Process., 55(2), 2019, 417-425

421

where $\varphi(CO)$ and $\varphi(CO_2)$ are the CO and CO_2 concentrations.
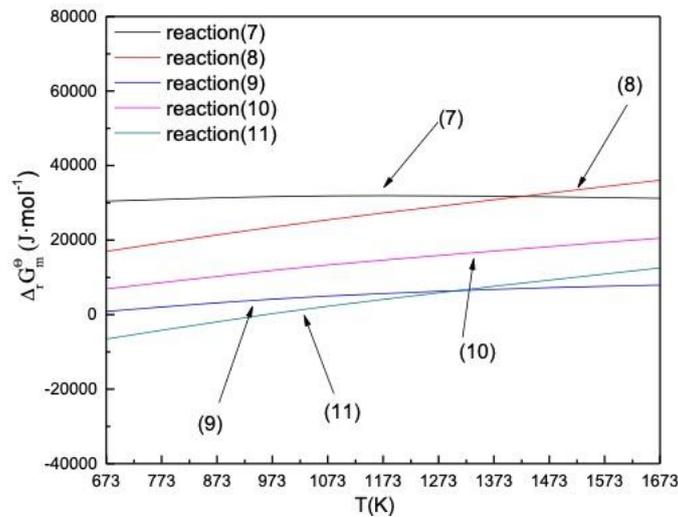
Fig. 4. Standard Gibbs free energy of ilmenite reduced by CO vs. temperature

Fig. 5 shows the equilibrium atmosphere for main reactions occurring during the reduction of ilmenite by CO with or without presence of MgO. The image shows that ilmenite reduction by CO without MgO is more difficult than that with MgO. This finding is due to the higher $\varphi(CO)$ required for ilmenite reduction to $FeTi_2O_5$ or TiO_2 (94% and 96%, respectively), whereas the $\varphi(CO)$ values for reduction to Mg_2TiO_4 and $MgTiO_3$ are 48% and 63%, respectively.
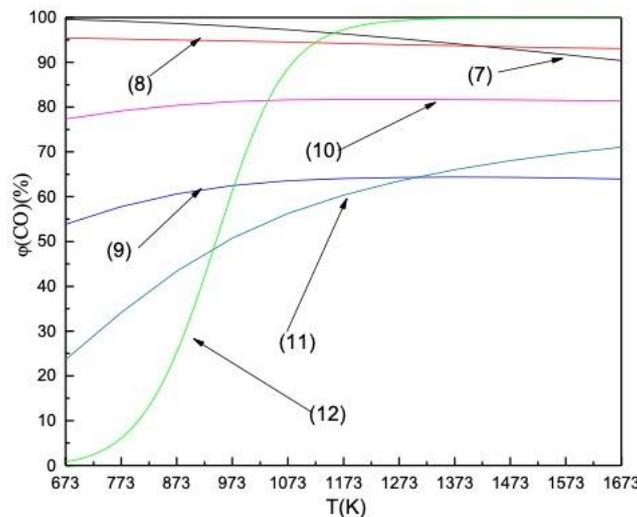
Fig. 5. Phase equilibrium diagram of ilmenite reduced by CO

3.2. Phase transformation of VTC briquettes at different Mg:Ti ratio and temperatures

Briquettes with different Mg:Ti ratios were heated at 1250°C under nitrogen flow for 60 min, and the phase transformations of the reduced VTC were investigated by XRD – the patterns are shown in Fig. 6. The main phases of reduction product, without addition of MgO (Mg:Ti=0), were metallic Fe and ferrous-pseudo-brookite ($FeTi_2O_5$), proving that magnetite in the VTC sample was completely reduced to Fe and that ilmenite was reduced to $FeTi_2O_5$ and Fe according to reaction (14). At a Mg:Ti ratio of 1 in the briquettes, the diffraction peaks of $FeTi_2O_5$ disappeared, and the main phases of reduced VTC turned into metallic Fe, $MgTiO_3$, and Mg_2TiO_4, indicating that ilmenite was reduced via reactions (15) and (16). No new phase, except excess of periclase (MgO), was observed in the reduced products in case of Mg:Ti=2 and 3. The traces of $MgTiO_3$ disappeared, and only Mg_2TiO_4 was detected under these conditions.

$$2FeTiO_{3(s)} + C(CO_{(g)})_{(s)} \rightarrow FeTi_2O_{5(s)} + Fe_{(s)} + CO(CO_2)_{(g)} \qquad (14)$$

$$FeTiO_{3(s)} + 2MgO_{(s)} + C(CO_{(g)}) \rightarrow Mg_2TiO_{4(s)} + Fe_{(s)} + CO(CO_2)_{(g)} \qquad (15)$$

$$FeTiO_{3(s)} + MgO_{(s)} + C(CO_{(g)}) \rightarrow MgTiO_{3(s)} + Fe_{(s)} + CO(CO_2)_{(g)} \qquad (16)$$
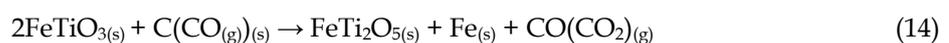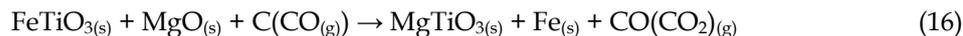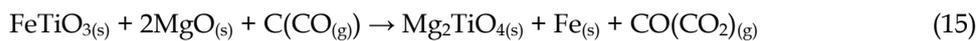
Fig. 7 shows the XRD patterns of VTC briquettes reduced by bituminous coal at different furnace temperature within 60 min. The main phases of the product reduced at 1050°C were metallic Fe and ilmenite (FeTiO₃), and no other titanium compounds were detected, indicating that the reduction of ilmenite did not occur at this temperature. The traces of Mg_2TiO_4 were observed in the sample reduced at 1150°C, and the diffraction peaks of $FeTiO_3$ weakened, proving that part of $FeTiO_3$ was reduced to Fe and Mg_2TiO_4 according to reaction (15). No new phase was observed, but the diffraction peaks of $FeTiO_3$ disappeared in the products reduced at 1250°C, representing that all of $FeTiO_3$ was completely reduced. When the furnace temperature reached 1350°C, $MgTi_2O_5$ was found in the reduction product, showing that reaction (17) occurred in this temperature.

$$FeTiO_{3(s)} + 1/2MgO_{(s)} + C(CO_{(g)}) \rightarrow 1/2MgTi_2O_{5(s)} + Fe_{(s)} + CO(CO_2)_{(g)} \qquad (17)$$
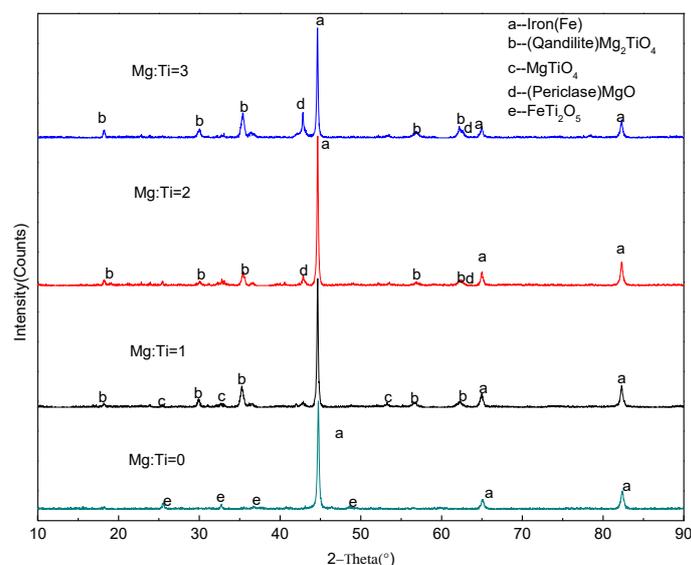
Fig. 6. XRD patterns of reduction products of VTC at different Mg:Ti ratio under 1250°C
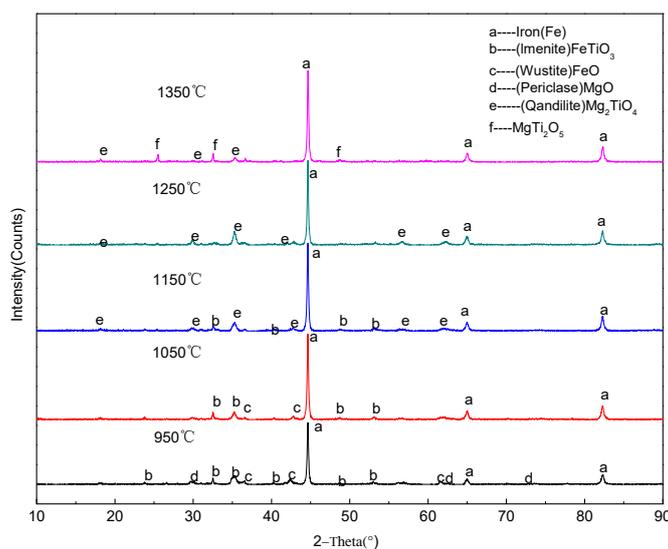
Fig. 7. XRD patterns of reduction products of VTC (Mg:Ti=2) obtained at different temperature

High-purity product is a primary requirement in the practical preparation of magnesium titanate. According to XRD analysis, three kinds of magnesium titanate were found in the reduced VTC, under different conditions. Among these types, $MgTi_2O_5$ presents the poorest dielectric properties, such as the characteristics of high crystallization capacity and dielectric loss, and is an unexpected phase in the

preparation of magnesium titanate ceramic, dielectric materials. Therefore, a Mg:Ti ratio of 2 and temperature of 1250°C are the optimal conditions to generate magnesium titanate material in the carbonthermic reduction of VTC.

3.3. Effect of temperature and Mg:Ti ratio on the degree of metallization

In order to comprehensively utilize iron and titanium resources, the preparation of magnesium titanate by the addition MgO, in the carbonthermic reduction of VTC, should ensure that the iron reduction can achieve good effect.

The VTC briquettes with a Mg:Ti ratio of 2 were reduced by bituminous coal at different temperature, and the degrees of metallization are shown in Fig. 8. The degree of metallization increased markedly from 900°C to 1250°C and reached a peak of 90.69% at 1250°C and then remained at about 90% with the temperature raising up to 1350 °C. It is suggested that the reduction of VTC briquettes with a Mg:Ti ratio of 2 may be the most effective between 1250°C to 1350°C.
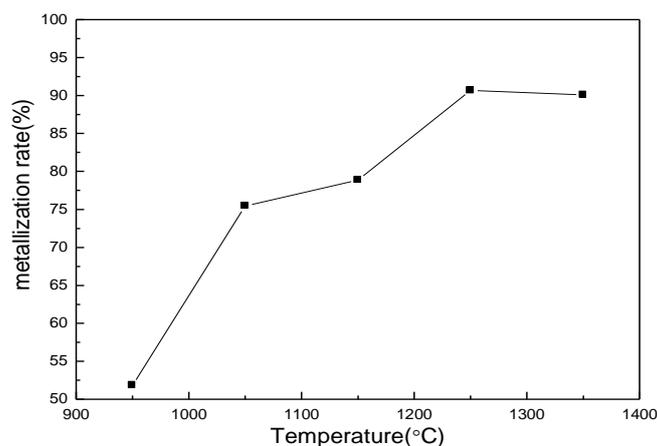
Fig. 8. The degree of metallization with different reduction temperature (Mg:Ti ratio of 2)
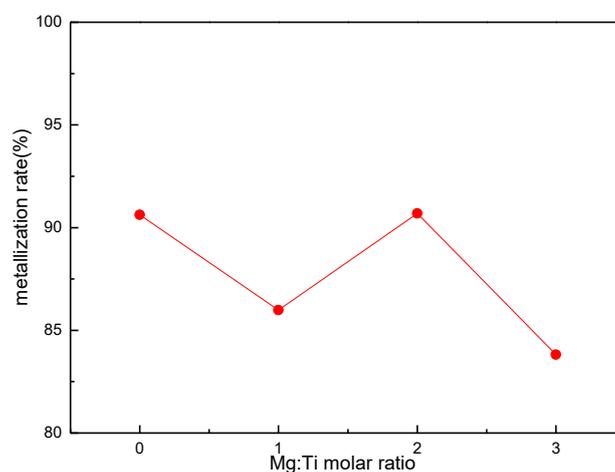
Fig. 9. The degree of metallization with different Mg:Ti ratio under 1250°C

Fig. 9 shows the degree of metallization of reduced VTC with different Mg:Ti ratio, heated at 1250°C within 60 min. Evidently, the degree of metallization curve presents a wave-shaped change and reached a high value at Mg:Ti ratios of 0 and 2. As proven, an appropriate amount of MgO can improve the reduction of VTC, whereas small or excessive MgO content exert an adverse impact to the reduction.

Coincidentally, a Mg:Ti ratio of 2 and temperature of 1250°C are also the optimal conditions to the reduction of iron oxide in VTC. This finding also indicates that the formation of magnesium titanate has no adverse effect on the proceeding of reduction.

3.4. Microstructure of reduced product

For an in-depth exploration of the generated magnesium titanate particles, SEM analysis was conducted to observe the microstructure and purity.

Fig. 10(a) shows the SEM mapping results of reduced product of the VTC under optimum conditions (temperature of 1250°C and Mg:Ti ratio of 2). Evidently, three main phases exist in the microstructural image, with the brightest and largest particles (position 1 in Fig. 10(a)) of metallic Fe connected together. The lighter particles (position 2 in Fig. 10(a)) are Mg_2TiO_4, manifesting as linear or strip inclusions between metallic Fe particles, except for a small amount of particles with a granular distribution. The last and darkest phase (position 3 in Fig. 10(a)) is the excess MgO, showing a unreacted portion of MgO in the reduction process. The energy-dispersive spectroscopy analysis results of three phases are shown in Fig. 10(b,c,d), revealing that the Mg_2TiO_4 particles were comparatively pure, except for the existing weak Fe peak, which indicate a small amount of unreacted iron oxide.
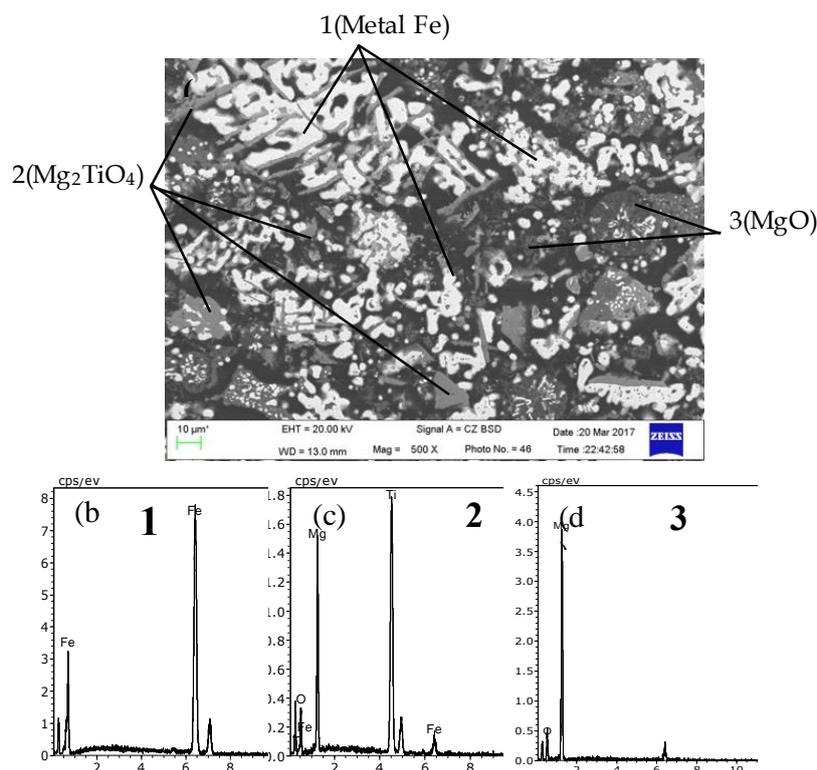
Fig. 10. EPMA mapping results (a) as well as the EDS spectra 1(b), 2(c) and 3(d) of reduction products of the VTC

4.   Conclusions

According to the thermodynamic analysis, magnesium titanate is feasible to be formed by the reaction of ilmenite and MgO under a reducing atmosphere. Moreover, ilmenite is more easily reduced by CO or carbon in the presence of MgO.

The effect of temperature and Mg:Ti ratio on the phase transformations and degree of metallization was investigated in the practical roast test. The temperature of 1250°C and Mg:Ti ratio of 2 are the optimum conditions to form magnesium titanate and reduce VTC pellets.

SEM analysis further confirmed the feasibility of the preparation of magnesium titanate by the addition of MgO in the carbonthermic reduction of vanadium titanomagnetite. On the other hand, trace Fe impurities were found in the magnesium titanate particles, indicating that further purification is required.

Acknowledgments

References

BALE, C.W., BELISLE, E., CHARTRAND, P., DECTEROV, S. A., ERIKSSON, G., HACK, K., JUNG, I.H., KANG, Y.B., MELANCON, J., PELTON, A.D., ROBELIN, C., PETERSEN, S., 2008. FactSage thermochemical software and databases — recent developments. Petersen: Calphad. 33, 296-311.

CHEN, D.S., SONG, B., WANG, L.N., QI, T., WANG, W. J., 2011. Direct reduction and enhanced reduction of vanadium- bearing titanomagnetite concentrates. J. Univ. Sci. Technol. B. 33, 1331-1336 (In Chinese).

CHEN, S.Y., CHU, M.S., 2014. Metalizing reduction and magnetic separation of vanadium titano-magnetite based on hot briquetting. Int. J. Miner. Met. Mater. 21, 225-233.

CHEN, S.Y., TANG, Y., CHU, S.M., GUO, P.H., HANG, Y.T., 2013. Reduction progress of vanadium titano-magnetite with coal powder. Chin. J. Peocess. 2, 236-240 (In Chinese).

DU, X.H., JIE, B., LOU, T.P., 2012. Research on solid reduction of vanadium-titanium magnetite. Northeast. Univ. 5, 685-688 (In Chinese).

FU, W.G., WE, Y.C, XIE, H.E., 2011. Development of intensified technologies of vanadium-bearing titanomagnetite smelting. J. Iron. Steel. Res. Int. 18, 7-10.

HU, T., LV, X.W., BAI, C.G., LUN, Z.G., QIU, G.B., 2014. Reduction behavior of panzhihua titanomagnetite concentrates with coal. Int. J. Miner. Met. Mater. 21, 252-260.

HUANG, Y., ZHOU, X.H., 2005. The synthesis of $MgTiO_3$ by solid state reaction and characteristics with addition. J. Funct. Mater. 36, 689-691.

LIU, S.S., GUO, Y.F., QIU, G.Z., JIANG, T., 2014. Solid-state reduction kinetics and mechanism of pre-oxidized vanadium−titanium magnetite concentrate. Trans. Nonferrous. Met. Soc. Chin. 10, 3372-3377.

LV, X., LUN, Z., YIN, J., BAI, C., 2013. Carbothermic reduction of vanadium titanomagnetite by microwave irradiation and smelting behavior. ISIJ. Int. 53, 1115-1119.

OVCHAR, O.V., V'YUNOV, O.I., DURILIN, D.A., STUPIN, Y.D., BELOUS, A.G., 2004. Synthesis and microwave dielectric properties of $MgO-TiO_2-SiO_2$ ceramics. Inorg. Mater. 40, 1116-1121.

PAUNOVA, R., 2002. Thermodynamic study of the reduction of titanium magnetite concentrate with solid carbon. Metall. Mater. Trans. B. 33, 633-638.

SREEDJAR, K., PAVASKAR, N.R., 2002. Synthesis of $MgTiO_3$ and $Mg_4Nb_2O_9$ using stoichiometrically excess MgO. Mater. Lett. 53, 452-455.

SUN, Y., ZHENG, H., DONG, Y., JIANG, X., SHEN, Y., SHEN, F., 2015. Melting and separation behavior of slag and metal phases in metallized pellets obtained from the direct-reduction process of vanadium-bearing titanomagnetite. Int J. Miner. Process. 142, 119-124.

ZHAO, L.S., WANG, L.N., CHEN, D.S., ZHAO, H.X., LIU, Y.H., TAO, Q.I., 2015. Behaviors of vanadium and chromium in coal-based direct reduction of high-chromium vanadium-bearing titanomagnetite concentrates followed by magnetic separation. Nonferrous Met. Soc. China. 25, 1325-1333.