Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 20(2010) 128−134
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Composition of off-gas produced by combined fluidized bed chlorination for preparation of $TiCl_4$

XIONG Shao-feng(熊绍锋)[1, 2, 3], YUAN Zhang-fu(袁章福)[1, 2], XU Cong(徐 聪)[4], XI Liang(席 亮)[3]

1. State Key Laboratory of Multiphase and Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China;
2. Department of Energy and Resources Engineering, College of Engineering, Peking University, Beijing 100871, China;
3. Graduate University of Chinese Academy of Sciences, Beijing 100049, China;
4. Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China;

Received 17 December 2008; accepted 25 March 2009

Abstract: The effects of carbon/slag molar ratio, chloride amount and temperature on equilibrium molar ratio (R_{Eq}) of CO to CO_2 for off-gas produced by carbochlorination of titanium slag were firstly investigated by thermodynamic calculation of equilibrium components of off-gas. The experimental CO/CO_2 molar ratio (R_{Ex}) was then obtained to be 0.2−0.3 by the carbochlorination experiment using a novel combined fluidized bed as chlorination reactor. To further investigate the reaction effect of the novel process mentioned above, R_{Ex}, R_{Eq} and corresponding reference data (R_{Re}) were compared. The results indicate that R_{Ex} is similar to R_{Re} (0.5−1.2) but different from R_{Eq} ($\geqslant$4.3), which is consistent with anticipation of R_{Ex} for the novel combined fluidized bed. The difference between R_{Ex} and corresponding R_{Eq} is mainly attributed to short retention time (about 1 s) of materials in combined fluidized bed and carbochlorination of oxide impurities contained in titanium slag, such as CaO, MgO and SiO_2.

Key words: titanium slag; equilibrium component; combined fluidized bed; carbochlorination

1 Introduction

Titanium resources from Panzhihua (Sichuan Province in China) are very rich and vanadic titanomagnetite reserves were proven to be 9.66×10^8 t, ranking first in the world. However, even after separation of iron and vanadium, 95% titanium resources cannot be used directly as the starting materials for preparation of titanium tetrachloride ($TiCl_4$) by fluidized chlorination bed[1]. One of the major reasons is high total content of CaO and MgO impurities (6%−9%, mass fraction) beyond the suitable range of 0.5%−1.0% for the commercial production of $TiCl_4$ to easily cause bed-agglomerate[1−3]. Several methods, such as chlorination in molten salt[4], chlorination in higher reaction temperature[4] and lower reaction temperature[5], have been proposed for anti-agglomeration. However, these methods were respectively confronted with inevitable problems in terms of environmental hazards, erosion of chlorinated reactor or increasing cost.

A method for anti-agglomeration without these shortcomings mentioned above was proposed using a novel combined fluidized bed as chlorination reactor[6−8]. A series of corresponding researches had been processed according to the combined fluidized bed, such as one-dimensional model for optimal technological parameters[6−7] and verification of effect of anti-agglomeration on an experimental scale[8]. However, the components, especially the CO/CO_2 molar ratio, of off-gas released from chlorination fluidized bed need to be further investigated.

CO/CO_2 molar ratio is one of the major parameters in the fluidized chlorination process, which reflects theoretical carbon consumption, thermal effect, etc[9]. Furthermore, CO/CO_2 molar ratio is correlated with the efficiency of carbochlorination of TiO_2. WANG and MA[9] compared CO/CO_2 equilibrium molar ratio with that of off-gas produced by carbochlorination of titanium

Foundation item: Project(2008AA06Z1071) supported by the High-tech Research and Development Program of China; Project(20306030) supported by the National Natural Science Foundation of China
Corresponding author: YUAN Zhang-fu; Tel/Fax: +86-10-82529077; E-mail: afuyuan@coe.pku.edu.cn
DOI: 10.1016/S1003-6326(09)60109-6

slag respectively corresponding to fluidized bed, molten salt chlorinating process and shaft furnace. However, the factors influencing the CO/CO_2 molar ratio were not discussed roundly. LIN and LEE[10], and YAGI and OKUDAIRA[11] investigated the relationship of temperature and CO/CO_2 molar ratio of off-gas produced by carbochlorination of rutile ($w(TiO_2) \geqslant 96\%$). However, the relationship may be not fit for the carbochlorination of titanium slag ($w(TiO_2)$=78%−83%). Up to now, few studies have been devoted to the relationship of CO/CO_2 molar ratio of off-gas and its equilibrium data under different technological conditions according to fluidized chlorination process of titanium slag. In addition, the relationship of CO/CO_2 molar ratio with reaction effect, theoretical carbon consumption, thermal effect, etc., for conventional fluidized bed may be invalid to be employed as reference for the novel combined fluidized bed due to their constructional difference. CO/CO_2 molar ratio for the novel fluidized bed needs to be further investigated.

In this study, the experimental CO/CO_2 molar ratio (R_{Ex}) was gained by carbochlorination of Panzhihua titanium slag in the novel combined fluidized bed. At the same time, HSC software was employed to calculate equilibrium components and the CO/CO_2 equilibrium molar ratio (R_{Eq}) under different technological conditions. R_{Ex} was further compared with R_{Eq} to evaluate reaction conversion.

2 Experimental

Panzhihua titanium slag with particle size of about 70−150 μm, as described in Table 1, was used as starting material. Petrocoke with particle size of about 500−850 μm, as described in Table 2, was provided by Panzhihua Steel & Iron Group, China, for premix with titanium slag. Off-gas discharged from TiO_2-preparing working section was used as chloride and its composition is listed in Table 3.

Table 1 Composition of Panzhihua titanium slag (mass fraction, %)

TiO_2	FeO	CaO	MgO	SiO_2	Al_2O_3	MnO	Others
76.76	5.02	1.72	7.37	4.70	2.15	0.832	1.448

Table 2 Chemical composition of petrocoke (mass fraction, %)

Volatile matter	Ash	Fixed carbon	H_2O
3.89	0.66	95.25	0.2

Table 3 Composition of oxidation off-gas (volume fraction, %)

Cl_2	O_2	CO	CO_2	N_2	HCl	Other
75	8	0.9	3.2	10.6	2.24	0.06

Schematic diagram of the experimental technological process is shown in Fig.1. The reactor may be composed of one or more parts, each of which consists of a riser with the inner diameter of 22 mm and a semi-circulating fluidized bed (SCFB) with the inner diameter of 59 mm. K-type temperature thermocouple was employed. The mixture of titanium slag and petrocoke was added into the combined bed bottom at the solid materials speeding rate of 120−450 g/min. Other technological parameters were shown in previous work[6−8] including that temperature range was between 923.15 and 1 273.15 K and gas apparent velocity was between 0.7 and 1.1 m/s.

Furnace slag was discharged regularly. Off-gas and powder discharged from top of combined fluidized bed and then entered condenser through cyclone for separating gases with different boiling points. The gases with low boiling point, such as $TiCl_4$, $SiCl_4$, VCl_3 and $VOCl_3$, became condensed and were collected in liquid

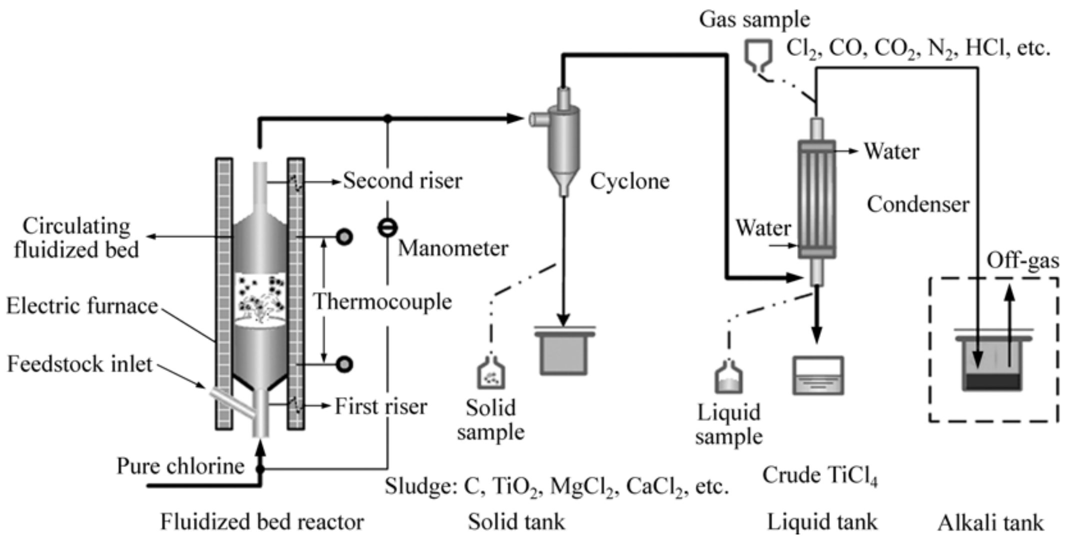

Fig.1 Schematic diagram of experimental process

tank for further purification. The gases with high boiling point, such as CO, CO_2, N_2, HCl and a small amount of Cl_2, passed through condenser top where off-gas was sampled and further disposed in alkali tank apparatus before venting to the atmosphere.

The components of off-gas were measured by Orsat gas analyzer. The morphology and components of furnace slag were analyzed by JSM−646LV scanning electron microscope with an energy-dispersive spectrometer (SEM-EDS).

3 Thermodynamic calculation

There exist the following main reactions in the course of carbochlorination of titanium slag:

$$TiO_2+2C+2Cl_2=TiCl_4+2CO \quad (1)$$

$$TiO_2+C+2Cl_2=TiCl_4+CO_2 \quad (2)$$

$$C+CO_2=2CO \quad (3)$$

Eq.(3) shows the gasification of carbon. Eq.(4) can be derived as follows by combination of Eqs.(1), (2) and (3), which totally expresses the quantitative relation of all the components:

$$TiO_2+2(1+R)/(R+2)C+2Cl_2= TiCl_4+2R/(R+2)CO+2/(R+2)CO_2 \quad (4)$$

where R is the CO/CO_2 molar ratio of off-gas.
The carbochlorination reactions of oxide impurities in titanium slag, such as MgO and CaO, are shown as follows:

$$MgO+C+Cl_2=MgCl_2+CO \quad (5)$$

$$2MgO+C+2Cl_2=2MgCl_2+CO_2 \quad (6)$$

$$CaO+C+Cl_2=CaCl_2+CO \quad (7)$$

$$2CaO+C+2Cl_2=2CaCl_2+CO_2 \quad (8)$$

Chemical equilibrium calculations of the TiO_2-C-Cl_2 reaction system were performed by the HSC program (Version 1.1)[12]. This mechanism of the program is based on the minimization of Gibbs free energy. The HSC database consists of enthalpy (H), entropy (S) and heat capacity (C) data of above 5600 species mainly according to the handbook edited by BARNER and SCHEURMAN[13].

The calculation reliability of HSC software can be testified by comparison of the results calculated by HSC with the results simultaneously calculated by other software for a certain system. The equilibrium product components of directly chlorinated reaction of TiO_2 were calculated herein by both HSC and NASA CEA program [5] and the results were compared, which are shown in Table 4. All the coefficients of correlation are close to 1, which indicates the reliability of HSC.

The chemical equilibrium calculations were processed to investigate the effects of temperature and molar ratio of starting materials on R_{Eq}. The components of impurities in titanium slag were considered according to the components of Panzhihua titanium slag as described in Table 1. The effect of $n(Cl_2):n(TiO_2)$ was investigated by means that R_{Eq} correlated to different $n(C):n(TiO_2)$ in the range of 1.6:1 to 2.6:1 was calculated at constant $n(Cl_2):n(TiO_2)$. Similarly, the effect of $n(Cl_2):n(TiO_2)$ on R_{Eq} was investigated.

Table 4 Simulated equilibrium molar fractions of reaction system of Cl_2 and TiO_2 for direct preparation of $TiCl_4$ at various temperatures

Component	Software	Molar fraction/%						Correlation coefficient
		573.15 K	673.15 K	873.15 K	1 073.15 K	1 273.15 K	1 473.15 K	
Cl	NASA	0	0	0.003	0.071	0.637	3.130	0.9999
	HSC	0	0	0.003	0.07	0.623	3.057	
ClO	NASA	0	0	0	0	0.002	0.011	0.9999
	HSC	0	0	0	0	0.002	0.012	
Cl_2	NASA	66.667	66.667	66.667	66.650	66.472	65.505	0.9988
	HSC	66.667	66.667	66.653	66.489	65.466	62.133	
O_2	NASA	0	0	0.01	0.102	0.471	1.368	0.9999
	HSC	0	0	0.011	0.108	0.509	1.464	
$TiCl_4$	NASA	0	0	0.01	0.102	0.472	1.374	0.9999
	HSC	0	0	0.011	0.108	0.510	1.5	
TiO_2	NASA	33.333	33.333	33.333	33.326	33.254	32.912	0.9937
	HSC	33.333	33.333	33.322	33.225	32.889	31.833	

Initial amounts of Cl_2 and TiO_2 are 2 mol and 1 mol, respectively.

4 Calculated results and discussion

4.1 Effect of temperature on equilibrium components and R_{Eq}

In the thermodynamic point of view, reaction temperature is the main factor influencing the equilibrium state correlated to CO/CO_2 molar ratio. Fig.2(a) shows the calculated result of equilibrium components under the conditions: $n(Cl_2):n(C):n(TiO_2)$ of 2.0:2.2:1.0 and pressure of 102.1 kPa. The equilibrium molar fraction of CO_2 and $TiCl_4$ in off-gas was very high below 873 K and decreased with the enlargement of the temperature until undergoing the turning point where CO became dominant above 1 000 K. Therefore, R_{Eq} increased with temperature in the range of 673−1 073 K. The result is consistent with the results given by ARTHUR[14] that the effect of reaction temperature on R_{Eq} for carbochlorination of TiO_2 was similar to that for the gasification of carbon.

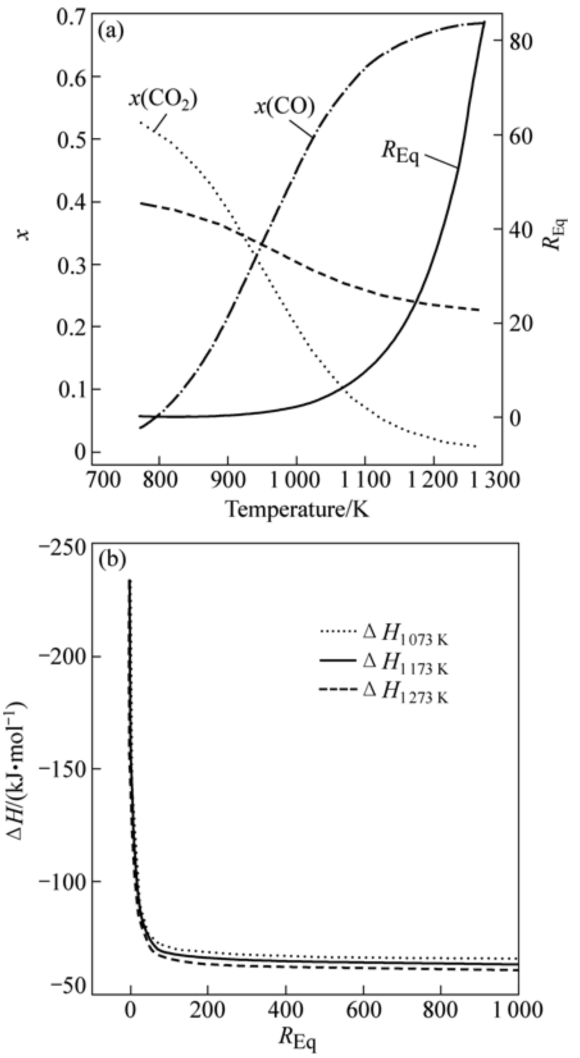

Fig.2 Effect of temperature on R_{Eq} and equilibrium components of off-gas (a) and relationship between R_{Eq} and reaction enthalpy corresponding to Eq.(4) (b)

Fig.2(b) shows the relationship between R_{Eq} and reaction enthalpy corresponding to Eq.(4) at various temperatures. At first, it indicates that the thermal effects increased with increasing the temperature in the range of 1 073−1 273 K. In addition, the thermal effect of reaction totally occurred according to Eq.(2) (the ordinate for R_{Eq}=0 as shown in Fig.2(b)) is apparently greater than that according to Eq.(1) (the ordinate for $R_{\mathrm{Eq}}\to+\infty$ as shown in Fig.2(b)). Therefore, the corresponding relationship between R_{Eq} and reaction enthalpy may be revealed by a phenomenon that the reaction enthalpy decreases with increasing R_{Eq}. It can be employed to explain the application of technique with 'low R_{Eq}' for the purpose of energy-saving in practical production process, in which both carbon and titanium slags were reduced and even somewhat oxygen was pumped in chlorinator for enabling the carbochlorination of TiO_2 to occur according to Eq.(3) with a low R_{Eq} to produce a large amount of CO_2 and maintain the furnace temperature.

4.2 Effect of carbon/slag ratio on R_{Eq}

Carbon/slag ratio can be represented by $n(C):n(TiO_2)$ and its effect on R_{Eq} at different temperatures is shown in Fig.3. R_{Eq} kept increasing with increasing $n(C):n(TiO_2)$ from 1.5:1 to 2.2:1. The results indicate that the incomplete gasification caused by excess carbon, above 2:1, was one of the main reasons of the higher equilibrium molar fraction of CO in off-gas, which further aroused the increase of R_{Eq}.

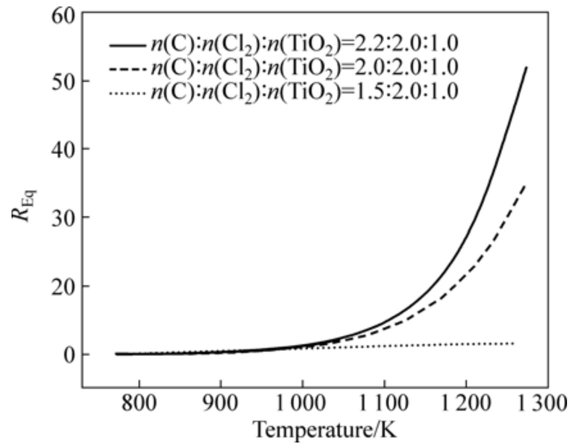

Fig.3 Effect of carbon/slag molar ratio on R_{Eq}

4.3 Effect of chlorine/slag ratio on R_{Eq}

Fig.4 shows the effect of $n(Cl_2):n(TiO_2)$ at various temperatures and initial $n(C):n(TiO_2)$=2.2:1.0 which is in excess of stoichiometry to facilitate a complete conversion of TiO_2. R_{Eq} increased simultaneously with the decrease of $n(Cl_2):n(TiO_2)$ in the range from 2.0:1.0 to 3.0:1.0.

The effect of the ratio of carbon/slag and chlorine

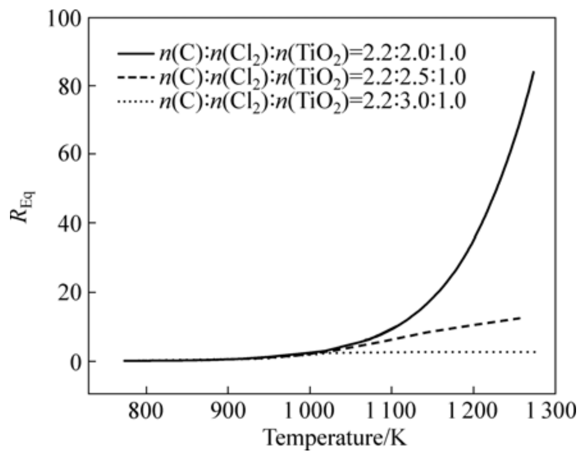

Fig.4 Effect of chlorine/slag molar ratio on R_{Eq}

amount can be contributed to three main reasons. Firstly, the existence of oxide impurities in titanium slag led to variance of R_{Eq} of off-gas in view that the CO/CO_2 molar ratio of product gas is different from R_{Eq}. Secondly, the initial molar ratio of CO to CO_2 contained in oxidation chlorinate, about 0.28, would be different from R_{Eq} in most cases, which had an influence on R_{Eq}. The more the oxidation chlorinate pumped in fluidized bed, the greater the influence on R_{Eq}. Thirdly, the carbochlorination of low-valent titanium oxide, such as TiO and Ti_3O_5, contained in titanium slag, was easier to occur according to SERYAKOV and BAKS[15] and COLEY et al[16]. The corresponding reactions are shown as follows:

$$TiO+C+2Cl_2=TiCl_4+CO \quad (10)$$

$$2TiO+2Cl_2=TiCl_4+TiO_2 \quad (11)$$

$$Ti_3O_5+5C+6Cl_2=3TiCl_4+5CO \quad (12)$$

$$2Ti_3O_5+2Cl_2=TiCl_4+5TiO_2 \quad (13)$$

The reactions indicate that carbochlorination of low-valent titanium oxide led to the increase of R_{Eq}.

5 Experimental results and discussion

Carbon/slag molar ratio (n(C):n(TiO_2)) can be adjusted by change of petrocoke mass fraction (slag/coke) in solid mixture whereas amount of chlorine (n(Cl_2):n(TiO_2)) can be adjusted by change of the gas apparent velocity of chlorine (v_g) and amount of solid mixture at the inlet (G_s) to optimize experimental effect. The experiment was herein carried out under technological conditions of reaction temperature range of 973−1 073 K, v_g=0.9 m/s, G_s=5.8 kg/h and mass ratio of slag to coke of 100:30, which was corresponding to the initial material molar ratio n(C):n(Cl_2):n(TiO_2)= 2.2:2.0:1.0.

WANG and MA[9] compared R_{Eq} with CO/CO_2 molar ratio (R_{Re}) of off-gas produced respectively by technological processes with fluidized bed, molten salt chlorination and shaft furnace with the assistance of some references. The comparison shows that R_{Re} of shaft furnace is the datum most close to R_{Eq}; R_{Re} of molten salt chlorination is lower and R_{Re} of fluidized bed is the minimum. In view of the analysis mentioned above, it is predicted that R_{Ex} corresponding to carbochlorination of titanium slag with novel combined fluidized bed should be different from R_{Eq}.

The conversion of TiO_2 (x(TiO_2)) increased with increasing R_{Ex}, as shown in Fig.5(a), which remains increasing with increasing temperature in the range of 973−1 073 K. Therefore, R_{Ex} can be also used as a reference for evaluating x(TiO_2).

Comparison of R_{Ex}, R_{Re} and R_{Eq} in the temperature range of 973−1 173 K is also shown in Fig.5(b). R_{Ex} is consistent with R_{Re} (0.5−1.2) with reference to YAGI and OKUDAIRA[11] but less than R_{Eq}.

The analysis of appearances and components of furnace slag is helpful for discovering what results in the difference between R_{Ex} and R_{Eq}. The polished furnace slag sample facilitated the observation and analysis of cross-sectional appearance of furnace slag as shown in Fig.6.

The reaction interface (RI) can be observed clearly and the content of titanium in unreacted slag interior

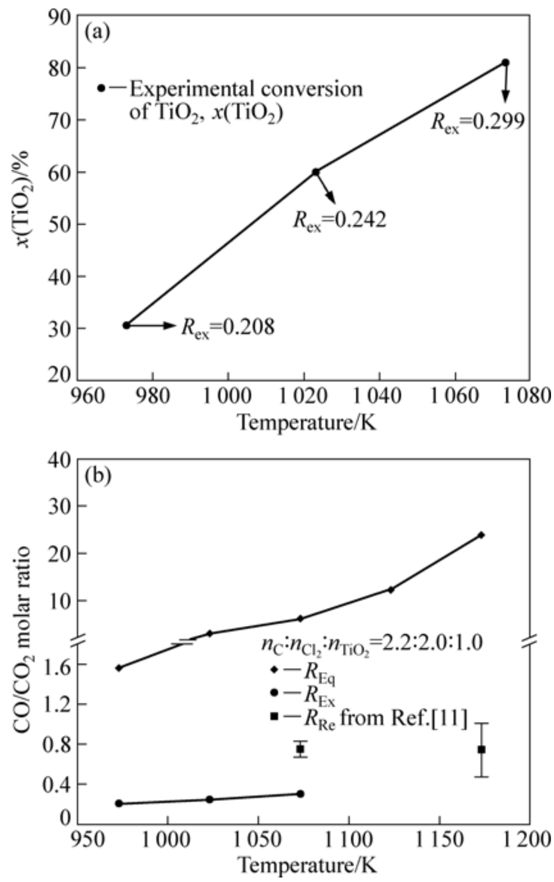

Fig.5 Analysis results of R_{Ex}: (a) relationship of conversion of TiO_2 and R_{Ex}; (b) Comparison of R_{Ex}, R_{Re} and R_{Eq}

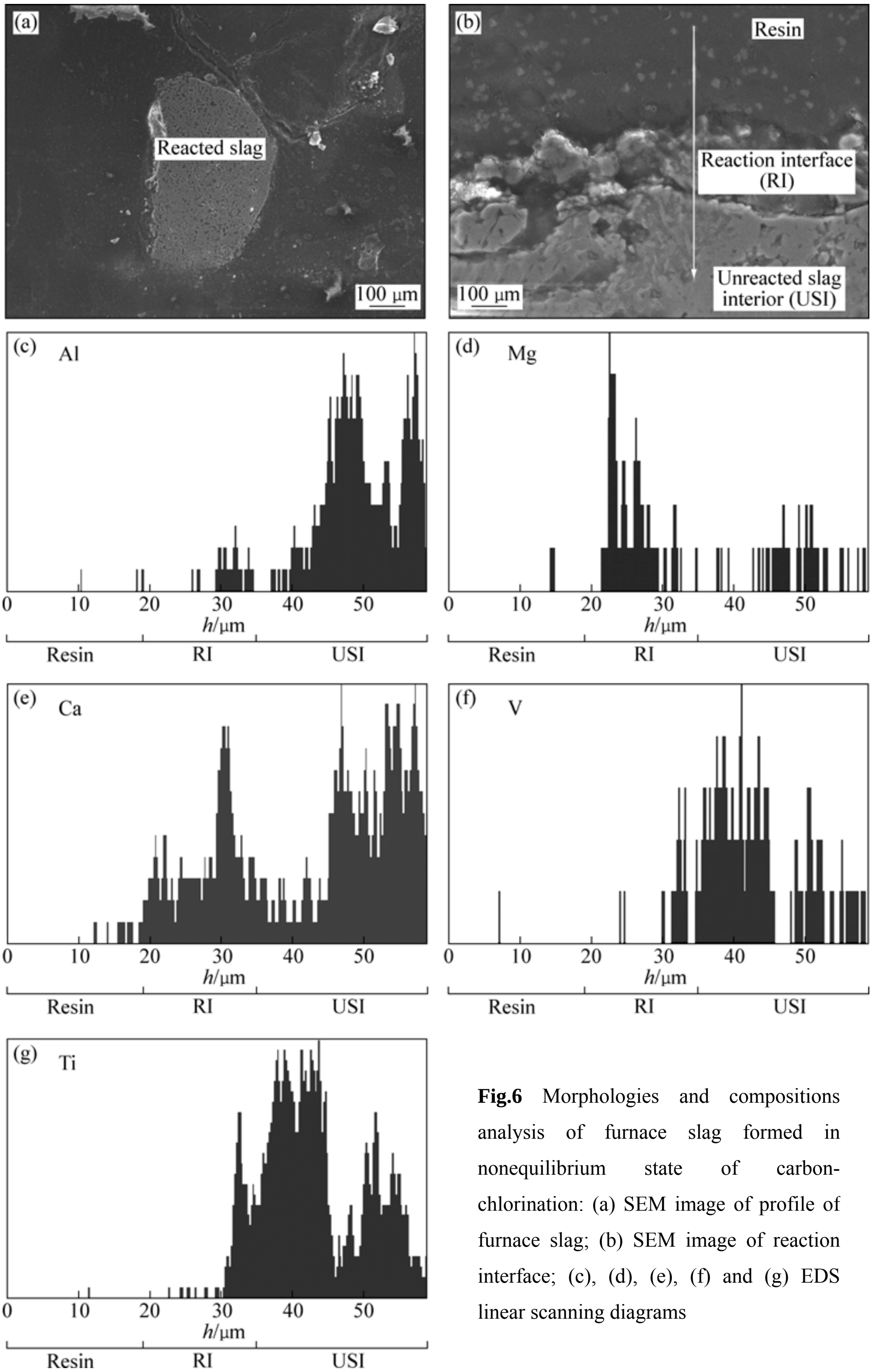

Fig.6 Morphologies and compositions analysis of furnace slag formed in nonequilibrium state of carbon-chlorination: (a) SEM image of profile of furnace slag; (b) SEM image of reaction interface; (c), (d), (e), (f) and (g) EDS linear scanning diagrams

(USI) is high. The results can be mainly due to short retention time (about 1 s) of starting materials in combined fluidized bed, which results in incomplete reaction and non-equilibrium state for carbochlorination of oxide contained in titanium slag and further leads to the variance of R_{Ex} with R_{Eq} of off-gas.

Besides, Figs.6(c)−(g) show that the elements, including Ca and Mg, were enriched in the surface area (i.e. reaction interface) of furnace slag where the content of element Ti is low. The results indicate that $TiCl_4$ produced by carbochlorination of TiO_2 on the surface of titanium slag evaporated up due to its low boiling point (409.55 K at 1.013 25$\times 10^5$ Pa) and left less in reaction interface. In view of the reaction priority of MgO and

CaO to TiO_2, the non-volatile substance containing enriched Ca and Mg in the surface area can be identified as the carbochlorination products of oxide impurities (i.e., $MgCl_2$, boiling point 1873.15 K at 1.013 25×10^5 Pa) and $CaCl_2$ (boiling point 1685.15 K at 1.013 25×10^5 Pa)), which existed as sticky liquid and left in surface area at about 1173 K. It is worthwhile to mention that the molar ratio of CO to CO_2 of product gas for the carbochlorination of oxide impurities, including CaO and MgO, is different from that for carbochlorination of TiO_2 under the same technological conditions and it would prevent R_{Ex} from getting access to R_{Eq} in some degree. Therefore, carbochlorination of oxide impurities in titanium slag may be another reason for the variance of R_{Ex} with R_{Eq} of off-gas.

6 Conclusions

1) The calculated results indicate that equilibrium molar ratio of CO to CO_2 increased with increasing carbon/slag molar ratio and reaction temperature but decreased with increasing chlorine amount. At the same time, the carbochlorination experiment for titanium slag was processed using novel combined fluidized bed as chlorinator and experimental molar ratio of CO to CO_2 of off-gas was obtained.

2) The comparison of experimental, equilibrium and referenced molar ratios shows that R_{Ex} (0.2−0.3) is nearly equal to R_{Re} (0.5−1.2) but less than R_{Eq} (⩾4.3).

3) Based on the analysis of appearances and components of furnace slag, the difference between R_{Ex} and R_{Eq} was mainly due to short retention time (about 1 s) of starting materials in combined fluidized bed and carbochlorination of oxide impurities in titanium slag.

References

[1] YUAN Z F, WANG X Q, XU C. A new process for comprehensive utilization of complex titania ore [J]. Minerals Engineering, 2006, 19(9): 975−978.

[2] LI J, ZHU Y, MA B. Study on the thermodynamics of oxidation of $TiCl_4$ and $AlCl_3$ in the chloride process for titanium white pigment [J]. Engineering Chemical Metallurgy, 1993, 14(4): 305−310.

[3] YUAN Z F, ZHOU J C, LIAO D H. Carburization and desulphurisation of the semi-steel during plasma heating [J]. Steel Research, 2002, 73(5): 175−179.

[4] MO Wei, DENG Guo-zhu, LUO Fang-cheng. Titanium metallurgy [M]. Beijing: Metallurgical Industry Press, 2006: 198−200. (in Chinese)

[5] YANG F, HLAVACEK V. Effect extraction of titanium from rutile by a low-temperature chloride process [J]. Reactors, Kinetics and Catalysis, 2000, 46(2): 355−366.

[6] XU Cong, YUAN Zhang-fu, XIAO Wen-ming. One-dimensional modeling of multiple-unit pneumatic transport reactor for producing titanium tetrachloride—Ⅰ. Mathematical model [J]. The Chinese Journal of Process Engineering, 2004, 4(6): 481−499. (in Chinese)

[7] XU Cong, YUAN Zhong-fu, WANG Xiao-qiang. One-dimensional model of a multiple-unit pneumatic transport reactor for producing titanium tetrachloride—Ⅱ. Simulated results on reactor behavior [J]. The Chinese Journal of Process Engineering, 2005, 5(1): 18−22. (in Chinese)

[8] XU C, YUAN Z F, WANG X Q. Preparation of $TiCl_4$ with the titanium slag containing magnesia and calcia in a combined fluidized bed [J]. Chinese Journal of Chemical Engineering, 2006, 14(3): 281−288.

[9] WANG He, MA Hui-juan. The composition of CO/CO_2 of off-gas produced by titanium-rich materials and the effect on technological process [J]. Vanadium Titanium, 1993，21(6): 16−19. (in Chinese)

[10] LIN C I, LEE T J. On the chlorination of titanium dioxide–carbon pellet Ⅰ. Effects of gas flowrate, reaction temperature, pellet size and pellet forming pressure [J]. Journal of the Chinese Institute of Chemical Engineers, 1985, 16(1): 49−55.

[11] YAGI S, OKUDAIRA S. Chlorination of rutile with the fluidized furnace [J]. Titanium, 1963, 11: 4−12. (in Japanese)

[12] KUBASCHEWSKI O. Metallurgical thermochemistry [M]. 5th ed. London: Pergamon Press, 1979: 282−288.

[13] BARNER H E, SCHEURMAN R V. Handbook of thermochemical data for compounds and aqueous species [M]. New York: John Wiley & Sons Inc, 1978: 176−194.

[14] ARTHUR J R. Reactions between carbon and oxygen [J]. Transactions of the Faraday Society, 1951, 47(1): 164−178.

[15] SERYAKOV G V, BAKS S A. High-temperature vaporization and thermodynamics of the titanium oxides [J]. Russian Journal of Inorganic Chemistry, 1967, 15(12): 3−7.

[16] COLEY K S, TERRY S B, GRIEVESON P. Simultaneous reduction and carburization of ilmenite [J]. Metallurgical and Materials Transactions, 1995, 26B(6): 485−494.

(Edited by YANG Hua)