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Study on Carbothermal Reduction of Titania in Molten Iron

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Abstract: In order to improve the reduction rate of titania in molten iron, various iron powders containing C, Si, Mn and S were melted. The experiments were carried out on the reduction of titania through a high-temperature tube furnace at 1,723–1,823 K. The quantitative effects of C, Si, Mn, S and temperature on the reduction of titania were investigated in the current study. The results demonstrated that when the carbon content, the manganese content and the temperature increased by 1 %, 0.1 % and 100 K, the reduction rate increased by 0.008 %/h, 0.001125 %/h and 0.0235 %/h, respectively; when the sulfur content increased by 0.01 %, the reduction rate decreased by 0.004875 %/h; the reduction rate was irregular with the change of silicon content in molten iron. The phase at the reaction interface after the experiment was confirmed to be the $Fe_2Ti_3O_9$ which was considered to be the combination product between iron oxide and titania; the lower titanium oxides were unstable and hard to be observed. The reduction was affected by the concentration of various elements in molten iron and the activity interaction coefficients between various elements. The rate constants for reduction were calculated at 1,723 K, 1,773 K and 1,823 K; the apparent activation energy was calculated as 209 kJ/mol through the rate constants and temperatures according to the Arrhenius equation.

Keywords: blast furnace, molten iron, titania, carbothermal reduction, reduction rate

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Introduction

In recent years, increased utilization of blast furnace (BF) has been highly desirable for ironmaking [1, 2]. Many companies have sustained a series of BF hearth incidents, such as the abnormal temperature increase of the hearth sidewall and the hearth sidewall breakout [3, 4]. Currently, the formation of a stable solidified layer, rapidly on the hot face of carbon bricks, is the key to solve the problems of the hearth, where the ore containing titania charged in BF is the most effective way to form a protective layer [5, 6]. Therefore, the titania reduction and the titanium behavior in molten iron have attracted an increasing attention.

Certain studies were executed to describe the reduction of titania. Licko et al. [7] analyzed the reduction of titania by carbon into lower titanium oxides beginning at 1,443 K. The sequence of reduction was observed: TiO_2-$Ti_nO_{2n\text{-}1}$ ($n > 10$)–Ti_nO_{2n-1} ($4 < n < 10$)–Ti_3O_5–(Ti_2O_3)–Ti(C_xO_y)–TiC(vacuum), whereas the Ti_2O_3 would be reduced and carburized to Ti(C_xO_y) rather than TiO [8]. Wei et al. [9] investigated that the titanium content in molten iron increased with the increase of titania in BF, binary basicity of slag, temperature, and reaction time. Zhao et al. [10] found that the titanium content in molten iron was mainly affected by the temperature. The reduction rate of titania in molten iron was strongly dependent on the carbon content and temperature [11]. Shigeno et al. [12] concluded that the reduction rate of titania would decline as sulfur adsorption at the interface decreased the contact area, when sulfur existed in molten iron. In contrast, the effect of sulfur was not apparently observed in the research of Bandyopadhyay [13]. The behavior of titanium in molten iron was investigated in other papers. Manabu et al. [14] reported that the swelling and drooping phenomena were observed when carbon saturated molten iron containing titanium. The effects of titanium content on viscosity, melting temperature and fluidity of molten iron were investigated by He et al. [15]. Wen [16] measured the viscosity of molten iron, observing that the effect of titanium was the most remarkable. In a number of studies, the reduction of titania was investigated; however, the effect of element

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content on the reduction is empirical summary, and few have carried out experiments to explore the quantitative effect of the elements on the reduction. Moreover, significant effort is required to analyze the reaction process through thermodynamic analysis and kinetics parameter calculation.

In this paper, the quantitative effect of the elements as well as the corresponding interaction on the reduction of titania in molten iron was investigated, and thermodynamic analysis and kinetics parameter calculation were analyzed to improve the reduction rate of titania to guide ironmaking practice.

Experimental procedure

Sample

In the present series of experiments, the titania powder (≥98 %), the iron powder (≥ 98 %), the graphite powder (≥ 99.85 %), the silica fume (≥ 99 %), the manganese powder (≥ 99.9 %) and the FeS (≥ 99 %) were utilized as the experimental raw materials.

The titania powder was ground to low-sized particles with an automatic grinding machine, in order to obtain a chemical uniform tablet. The size distribution and specific surface area of titania particles were measured with a laser particle size analyzer (LMS-30), as presented in Table 1. Consequently, the pure titania powder (10 g in weight) was pressed into a tablet (retained 3 min under 300 MPa of pressure) of 10 mm in thickness and 25 mm in diameter. Subsequently, the titania sample was placed in a drying oven at 378 K for 2 h. Following this, the sample was pre-sintered in a high-temperature tube furnace at 1,823 K for 2 h, to increase the strength. The sintered titania sample was 8 mm in thickness and 20 mm in diameter (as presented in Figure 1), and the volume of sintered titania sample was reduced due to crystal transition.

Fine-grained reduced iron powder was the main experimental material utilized to melt into molten iron. In order to simulate the composition of molten iron in the actual BF, graphite powder, silica fume, manganese powder, and FeS (sulfur is volatile during heating) were mixed with the iron powder. The mixture was ground thoroughly with a mortal, in order to increase the contact between the particles, in order for the mixture to be completely melted when the temperature exceeds the corresponding liquidus temperature.

Table 1: Geometry parameters of titania particles.

Particle	Average particle size (μm)	Specific surface area (m^2/cm^3)
Titania	1.249	6.615

Reactor

A high-temperature tube furnace was employed for the heating of the materials to the desired temperature. The high-temperature tube furnace mainly consisted of two parts: the furnace body and the control cabinet. The schematic diagram of the furnace body is presented in Figure 2(a). The U-shaped $MoSi_2$ rod was utilized as the heating element. A Pt-6 %Rh/Pt-30 %Rh thermocouple was placed under the protection crucible. Prior to the experiment initiation, a standard thermocouple was utilized to measure the constant-temperature zone and calibrate the temperature of the thermocouple inside the furnace. The constant-temperature zone was approximately 8 cm in length, whereas the highest accuracy area (± 1 ℃) was located at 3 cm above the crucible supporter, in order for the temperature measurement by the Pt-6 %Rh/Pt-30 %Rh thermocouple to match the actual temperature of molten iron.

Experimental procedure

Approximately 160 g of the iron powder mixture was placed in an alumina crucible (36 mm I.D. and height 73 mm) or a graphite crucible (40 mm I.D. and height 80 mm). Consequently, the alumina crucible or the graphite crucible was placed into the protective crucible (67 mm I.D. and height 93 mm). The components of molten iron and experimental conditions of each experiment are presented in Table 2. The assemble was placed into the tube at room temperature and heated from room temperature to the desired temperature at a rate of 5 ℃/min. When the experiment started, high-purity argon gas (99.999 %) was introduced into the tube at a flow rate of 2 L/min, to protect the molten iron from potential reactions. When the temperature reached the desired value, the molten iron was stirred with a glass rod and the temperature was maintained for 30 min, to obtain a uniform composition of molten iron. Following this, the sintered titania sample was placed on the surface of molten iron through a thin iron wire (Figure2(b)). The reaction started and lasted for 120 min. Samples of molten iron were withdrawn with a

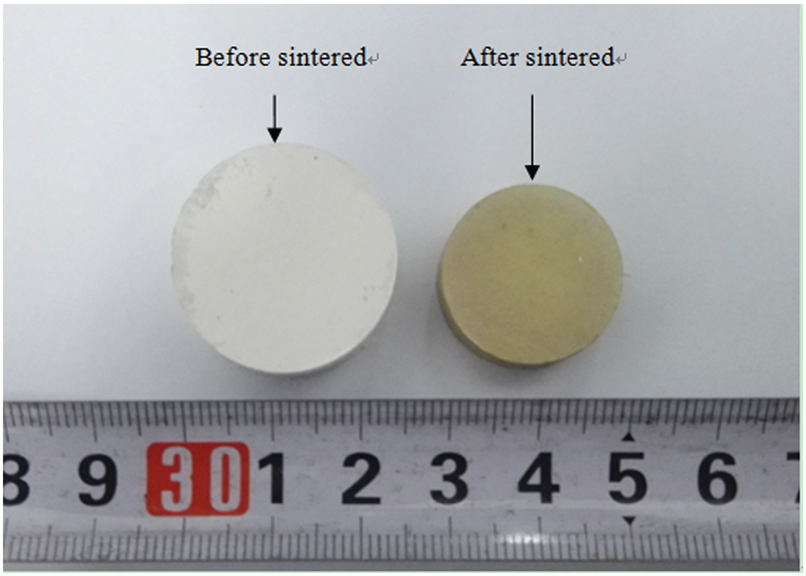

Figure 1: Titania sample prior to and following sintering.

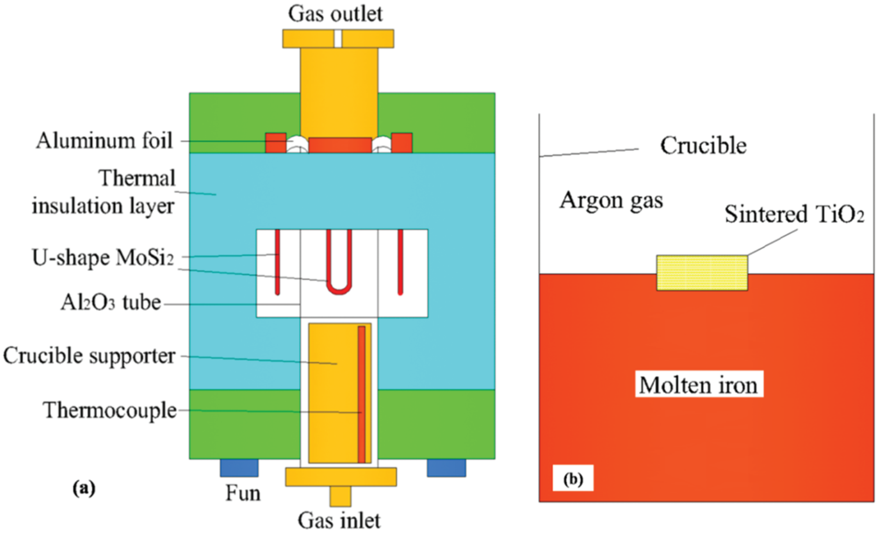

Figure 2: Schematic diagram of experimental apparatus.

glass tube (4 mm I.D.) every 30 min and quenched quickly in water for chemical analysis.

Results and discussion

Experimental results

Effect of element content in molten iron

Effects of different element contents in molten iron on the reduction of titania were investigated at 1,773 K. According to Figure 3, the titanium content in molten iron increased rapidly as the carbon content increased in the initial molten iron. The slope of each line corresponded to the reduction rate of titania. Therefore, it could be concluded that the reduction rate of titania increased along the higher carbon content. Figure 4 presents the reduction rate decreased along the increasing sulfur content. In a previous study [17], the surface tension of molten iron containing sulfur was measured, whereas the adsorption of sulfur was observed. The adsorption phenomenon of sulfur was considered to reduce the contact area between molten iron and solid titania inhibiting the reduction of titania.

Effect of silicon is presented in Figure 5. The reduction rate was irregular with the change of silicon content in molten iron, the reduction rate was high when the silicon content was 0.2 %, the reduction rate was maintained at a

Table 2: Chemical composition of molten iron and experimental conditions of each experiment.

Number	Fe, Wt Pct	C, Wt Pct	Si, Wt Pct	Mn, Wt Pct	S, Wt Pct	Crucible	Temperature, K
A-1	97.18	2.5	0.2	0.1	0.02	Alumina	1,773
A-2	96.18	3.5	0.2	0.1	0.02	Alumina	1,773
A-3	95.18	4.5	0.2	0.1	0.02	Alumina	1,773
A-4	94.68	Saturated	0.2	0.1	0.02	Graphite	1,773
B-1(A-3)	95.18	4.5	0.2	0.1	0.02	Alumina	1,773
B-2	95.16	4.5	0.2	0.1	0.04	Alumina	1,773
B-3	95.14	4.5	0.2	0.1	0.06	Alumina	1,773
C-1(A-3)	95.18	4.5	0.2	0.1	0.02	Alumina	1,773
C-2	94.98	4.5	0.4	0.1	0.02	Alumina	1,773
C-3	94.78	4.5	0.6	0.1	0.02	Alumina	1,773
D-1(A-3)	95.18	4.5	0.2	0.1	0.02	Alumina	1,773
D-2	94.98	4.5	0.2	0.3	0.02	Alumina	1,773
D-3	94.78	4.5	0.2	0.5	0.02	Alumina	1,773
E-1	94.68	Saturated	0.2	0.1	0.02	Graphite	1,723
E-2(A-4)	94.68	Saturated	0.2	0.1	0.02	Graphite	1,773
E-3	94.68	Saturated	0.2	0.1	0.02	Graphite	1,823

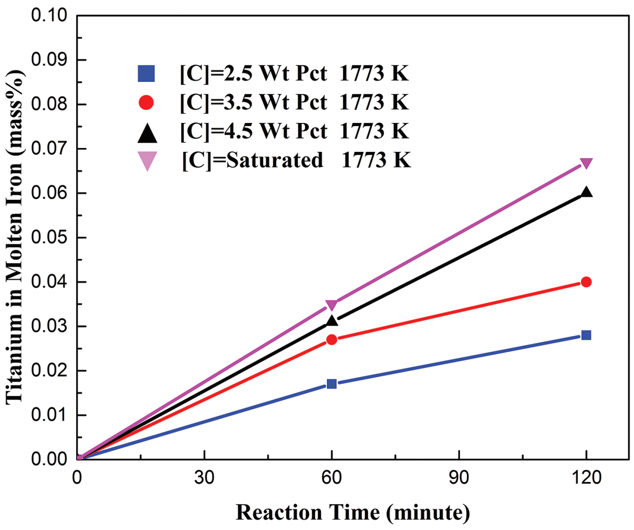

Figure 3: Effect of carbon content.

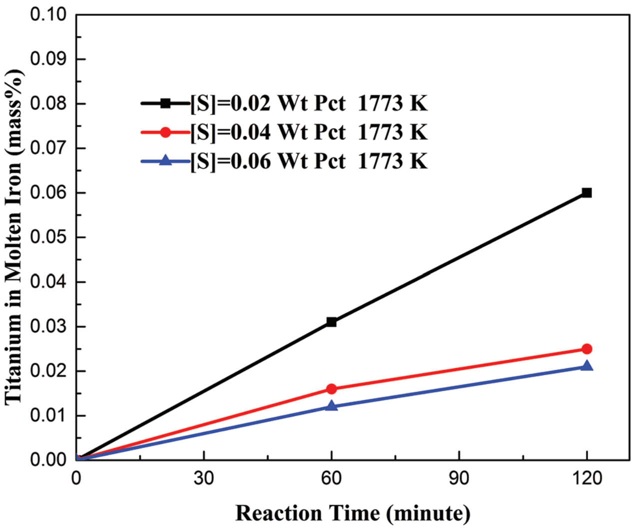

Figure 4: Effect of sulfur content.

low level when the silicon content was 0.4 % or 0.6 %. The reduction rate increased along with the higher manganese content in molten iron, as presented in Figure 6, which demonstrated that manganese was a promoter of the reduction. This occurred mainly because the manganese decreased the viscosity of molten iron and promoted the diffusion of carbon in the molten iron.

Effect of temperature

Effect of temperature on the reduction of titania was investigated under the condition of saturated carbon content at 1,723 K, 1,773 K and 1,823 K (as presented in Figure 7). According to the results, the reduction rate of titania increased rapidly along with the higher temperature. Firstly, the solubility of carbon in molten iron increased with the higher temperature and the activity of carbon increased in molten iron. Secondly, the viscosity of molten iron decreased with the increasing temperature, and the kinetic condition of mass transfer in molten iron was improved. Hence, the temperature had the highest effect on the reduction of titania in the molten iron.

As d[Ti]/dt indicated the reduction rate of titania, the reduction rate under different element content and temperature can be calculated as presented in Table 3. According to Table 3, when the carbon content increased by 1 %, the reduction rate increased by 0.008 %/h; when

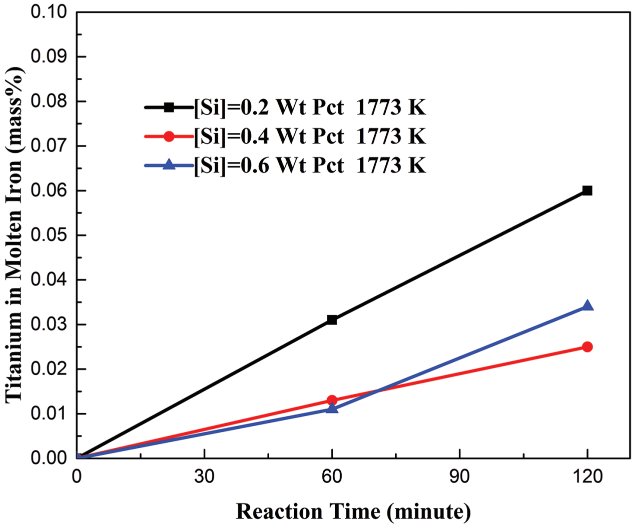

Figure 5: Effect of silicon content.

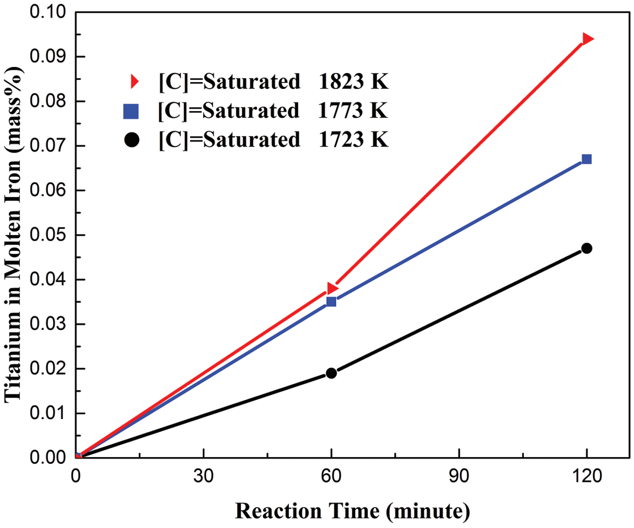

Figure 7: Effect of temperature.

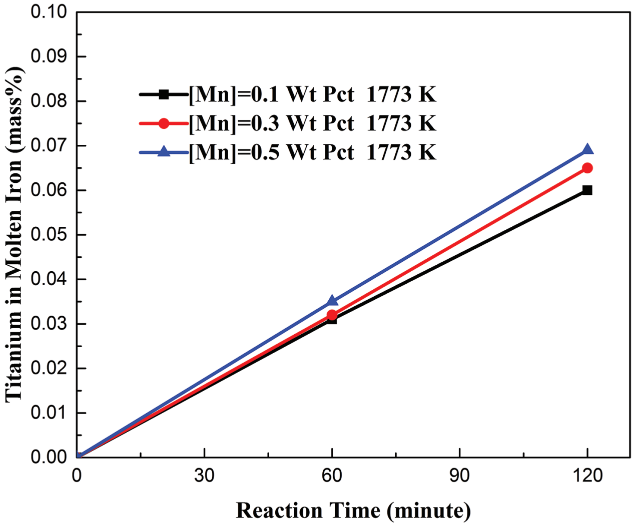

Figure 6: Effect of manganese content.

the sulfur content increased by 0.01 %, the reduction rate decreased by 0.004875 %/h; when the manganese content increased by 0.1 %, the reduction rate increased by 0.001125 %/h; when the temperature increased by 100 K, the reduction rate increased by 0.0235 %/h.

Analysis and discussion

Thermodynamic analysis

The overall reaction of the reduction of titania in molten iron can be expressed as follows:

$$(TiO_2) + 2[C] = [Ti] + 2CO \quad \Delta G^{\Theta} = 632210 - 302.09T(J/mol) \tag{1}$$

The carbothermal reduction of titania in molten iron was carried out step by step, where the reduction process was as follows: TiO_2–Ti_3O_5–Ti_2O_3–TiO–Ti. When the titania was completely reduced and a surplus of carbon still existed, the following reaction occurred:

$$[\mathrm{Ti}] + [\mathrm{C}] = \mathrm{TiC}_{(\mathrm{s})} \quad \Delta G^{\Theta} = -176,934 + 100.11T(\mathrm{J/mol}) \tag{2}$$

The remaining titania was observed subsequently to each experiment which proved that the titania was not been completely reduced. Therefore, reaction (2) could not occur and no TiC was found in the molten iron or the tablet.

The XRD (X-ray diffraction) analysis was conducted on the reaction interface of the sintered titania prior to and following the experiments. The results are presented in Figure 8. From Figure 8, the phase at the reaction interface after the experiment was confirmed to be the $Fe_2Ti_3O_9$(Fe_2O_3·$3TiO_2$), which was considered to be the combination product between iron oxide and titania. The lower titanium oxides were not observed in the reaction, and this phenomenon was in agreement with the results reported by certain studies [18, 19] because the lower titanium oxides were unstable. Also, certain peaks were confirmed as graphite carbon. It could be inferred that a transition layer might exist at the interface during the experiments.

Table 3: The reduction rate under different element contents and temperatures.

C	The element content, %	2.5	3.5	4.5	△[*C*] = 1
	The reduction rate, %/h	0.014	0.02	0.03	△rate = 0.008
S	The element content, %	0.02	0.04	0.06	△[*S*] = 0.01
	The reduction rate, %/h	0.03	0.0125	0.0105	△rate = 0.004875
Mn	The element content, %	0.1	0.3	0.5	△[Mn] = 0.1
	The reduction rate, %/h	0.03	0.0325	0.0345	△rate = 0.001125
Temperature	Temperature, K	1,723	1,773	1,823	△*T* = 100
	The reduction rate, %/h	0.0235	0.0335	0.047	△rate = 0.0235

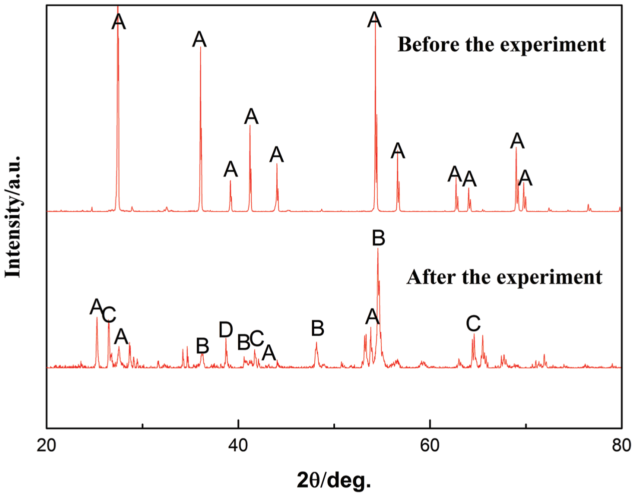

Figure 8: XRD pattern analysis prior to and following experimentation.

Effect of elements interaction on reduction

The equilibrium constant of reaction (1) can be expressed by:

$$K = \frac{a_{[\mathrm{Ti}]}(P_{\mathrm{co}}/P^{\Theta})^2}{a_{[\mathrm{TiO_2}]}a_{[\mathrm{C}]}^2} \tag{3}$$

where K is the equilibrium constant of the chemical reaction; $a_{[\mathrm{Ti}]}$ is the activity of titanium in molten iron; P_{co} is the partial pressure of CO; P is the normal atmospheric pressure; $a_{[\mathrm{TiO2}]}$ is the activity of solid titania which is usually considered to be 1 and $a_{[\mathrm{C}]}$ is the activity of carbon in molten iron.

When the overall reaction reaches equilibrium, the standard Gibbs-free energy of reaction (1) can also be expressed as:

$$\Delta G^{\Theta} = -RT\ln K = -2.303RT\lg K \tag{4}$$

For the equilibrium constant of reaction (1):

$$lg\ K = lg[\%Ti] + lg\ f_{Ti} + 2\lg(P_{co}/P^{\Theta}) - 2\lg[\%C] - 2\lg\ f_C \tag{5}$$

The titanium content in molten iron can be expressed by eq. (6) from eqs. (1), (4), and (5):

$$\begin{aligned} lg[\%Ti] = &-\frac{33018.50}{T} + 15.78 - \lg\ f_{Ti} - 2\lg(P_{co}/P^{\Theta}) \\ &+ 2lg[\%C] + 2lg\ f_C \end{aligned} \tag{6}$$

It is known from eq. (6) that the temperature had the highest effect on the titanium content in molten iron. The experimental results agreed with the calculation. In addition, the viscosity of molten iron decreased as the temperature increased, described as [20]:

$$\mu = 0.3699 \times 10^{-3} e^{\frac{41.4\times10^3}{R(T+273)}} \tag{7}$$

where R is the gas constant.

Therefore, the kinetic condition of the mass transfer in molten iron was improved. Secondly, the wettability between solid titania and molten iron also improved, which could increase the contact area. Furthermore, the carbon content in molten iron was also temperature dependent, increasing along with the higher temperature. Consequently, the higher amount of titanium could be obtained with the higher temperature.

The activity coefficient in eq. (6) can be calculated by eq. (8), according to the Wagner model [21]:

$$\lg\ f_{Ti} = e_{Ti}^{Ti}[\%Ti] + e_{Ti}^{C}[\%C] + e_{Ti}^{Si}[\%Si] + e_{Ti}^{Mn}[\%Mn] + e_{Ti}^{S}[\%S] \tag{8}$$

It was apparent from eqs. (6) and (8) that the titanium content in molten iron was affected by the concentration of various elements in the molten iron and the activity interaction coefficients among the various elements. The activity interaction coefficients among various elements at 1,873 K are presented in Table 4.

Table 4: Activity interaction coefficients among various elements at 1,873 K.

e_i^j	e_{Ti}^{Ti}	e_{Ti}^{C}	e_{Ti}^{Si}	e_{Ti}^{Mn}	e_{Ti}^{S}	e_{C}^{C}	e_{C}^{Si}	e_{C}^{Mn}	e_{C}^{S}
Numerical value	0.013	−0.165	0.05	0.0043	−0.11	0.14	0.08	−0.012	0.016

The activity coefficient of titanium decreased with the increasing carbon content (activity interaction coefficient is negative), so the reduction rate increased. The carbon content had a higher effect relatively to the other elements, as it had the highest activity interaction coefficient. The activity coefficient of titanium increased along with the higher manganese content, so the reduction rate should have decreased, while the reduction rate increased along with the higher manganese content; this occurred mainly because the manganese decreased the viscosity of molten iron and promoted the diffusion of carbon in the molten iron. The activity coefficient of titanium decreased along with the higher sulfur content (activity interaction coefficient is negative), so the reduction rate should have increased, while the reduction rate decreased along with the higher sulfur content; the adsorption phenomenon of sulfur was considered to reduce the contact area between molten iron and solid titania inhibiting the reduction of titania.

Kinetics parameter calculation

The activity of carbon in molten iron can be written as eq. (9), and the activity coefficient can be calculated through eq. (10):

$$a_{[C]} = [\%C]^{*} f_C \tag{9}$$

$$lg\ f_C = e_C^C[\%C] + e_C^{Si}[\%Si] + e_C^{Mn}[\%Mn] + e_C^S[\%S] \tag{10}$$

The activity interaction coefficients at different temperatures can be calculated through the activity interaction coefficients at 1,873 K:

$$e(T) = \frac{e \times 1,873}{T} \tag{11}$$

The activity of carbon under different carbon content at 1,773 K can be calculated, and $d[\mathrm{Ti}]/dt$ was linearly plotted against the activity of carbon in Figure 9. $d[\mathrm{Ti}]/dt$ indicated the reduction mass of titanium at unit time, that was the reduction rate of titania. Therefore, the reduction rate was linearly plotted against the activity of carbon.

Consequently, the rate constants for the reduction of titania can be calculated through eq. (12) [11]:

$$\frac{d[\mathrm{Ti}]}{dt} = \frac{A}{W} k_{[Ti]} a_{[C]} \tag{12}$$

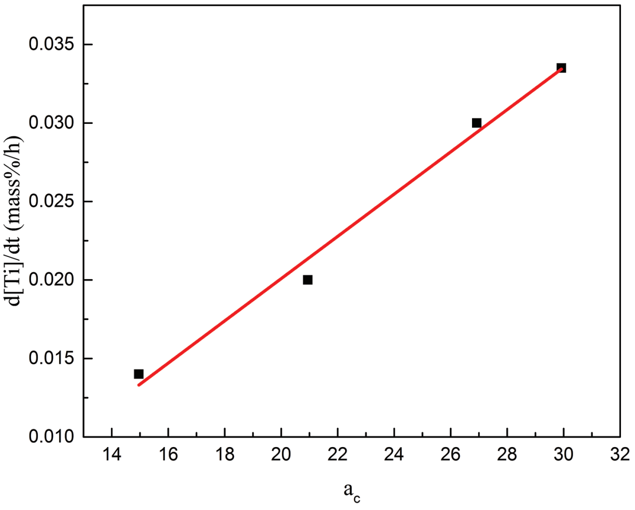

Figure 9: Relation between $d[\mathrm{Ti}]/dt$ and a_c at 1,773 K.

where [Ti] is the titanium content in molten iron, mass%; t is the reaction duration, h; A is the reaction area, m^2; W is the weight of molten iron, kg; $k_{[\mathrm{Ti}]}$ is the rate constant, kg m^{-2} h^{-1}; $a_{[\mathrm{C}]}$ is the activity of carbon in molten iron.

A transition layer might exist at the contact surface between the liquid and the solid as presented in Figure 11, whereas the mass transfer process resistance was concentrated in the transition layer. The exchange of substances was in equilibrium in the transition layer. The material flow density of the transport material component was proportional to the concentration difference of the component between the liquid and the transition layer. The fluid in the transition layer was stationary.

The rate constants for the reduction of titania could be calculated at 1,723 K, 1,773 K and 1,823 K through the aforementioned equations. The rate constant increased rapidly as the temperature increased, as presented in Table 5. Simultaneously, the apparent activation energy was calculated as 209 kJ/mol through the linear fitting of $\ln k_{[\mathrm{Ti}]}$ and T^{-1}, according to the Arrhenius equation (Figure 10).

Table 5: Rate constants for reduction of titania at 1,723 K, 1,773 K and 1,823 K.

Temperature, K	1,723	1,773	1,823
The rate constant, kg m^{-2} h^{-1}	0.471	0.713	1.05

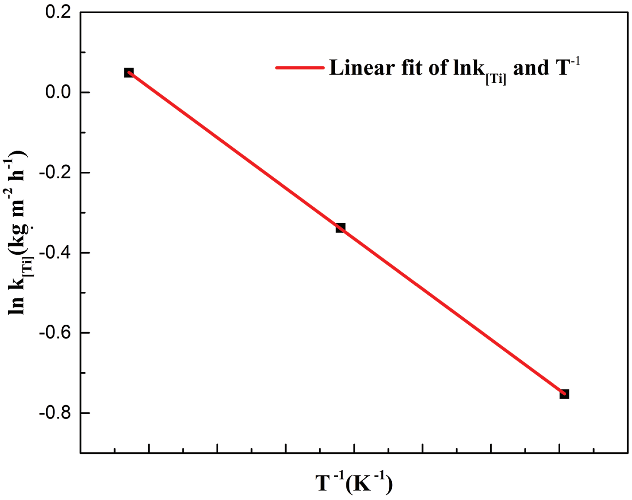

Figure 10: Linear fitting of $\ln k_{[Ti]}$ and T^{-1}.

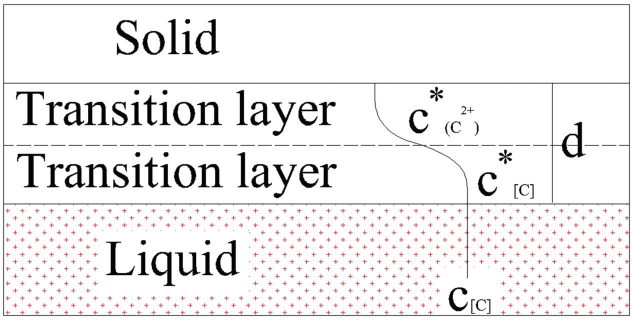

Figure 11: Explanatory view of transition layer.

Conclusions

In order to improve the reduction rate of titania in molten iron, experiments were carried out on the reduction of titania with a high-temperature tube furnace at 1,723–1,823 K. The following conclusions were obtained:

(1) When the carbon content, the manganese content and the temperature increased by 1 %, 0.1 % and 100 K, the reduction rate increased by 0.008 %/h, 0.001125 %/h and 0.0235 %/h, respectively; when the sulfur content increased by 0.01 %, the reduction rate decreased by 0.004875 %/h; the reduction rate was irregular with the change of silicon content in molten iron. The temperature had the highest effect on the reduction.

(2) The phase at the reaction interface after the experiment was confirmed to be the $Fe_2Ti_3O_9$ which was considered to be the combination product between iron oxide and titania; the lower titanium oxides were unstable and hard to be observed.

(3) The reduction was affected by the concentration of various elements in molten iron and the activity interaction coefficients between various elements.

(4) The rate constants for the reduction of titania were calculated at 1,723 K, 1,773 K and 1,823 K. The apparent activation energy was calculated as 209 kJ/mol through the rate constants and temperatures according to the Arrhenius equation.

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