

RATE OF SILICOTHERMIC REDUCTION OF TiO_2 IN TiO_2 CONTAINING SLAG MELT^①

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ABSTRACT A mathematic model was designed to describe and calculate the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag melt. Details of theoretical analysis and experimental test were presented. The rate of silicothermic reduction of TiO_2 in TiO_2 containing slag melt could be given by: $C(\text{TiO}_2) = C(\text{TiO}_2)_0 e^{-k't}$.

Key words mathematic model silicothermic reduction TiO_2 containing slag melt

1 INTRODUCTION

The silicothermic reduction process offers an attractive means of treating low TiO_2 containing slag. Ferrosilicon is used to reduce TiO_2 to titanium silicide. In some papers^[1], experimental data were reported on the reactions and thermodynamics of silicothermic reduction of TiO_2 containing slag melt. The metallic phase of the Ti-Fe-Si system and the slag of the TiO_2 -CaO- Al_2O_3 -MgO- SiO_2 system were analysed after TiO_2 had been reduced from the TiO_2 containing slag melt. The mixture of slag belonging to the system of TiO_2 -CaO- Al_2O_3 -MgO- SiO_2 , lime and ferrosilicon were heated and maintained in the temperature range of 1400~1700 °C. Ferrotitaniumsilicon (mainly TiSi_2) was obtained and identified in the metallic phase.

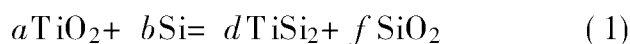
The overall reduction process involves not only the chemical reaction but also the mass transfer steps. The following mathematic model (see Fig. 1) has been developed to represent the overall reduction process.

2 MATHEMATIC MODEL

The rate of silicothermic reduction of TiO_2 was studied as a function of the following variables:

- (1) reduction time at constant temperature and amount of reducing agent;
- (2) amount of reducing agent at constant reduction time and temperature;
- (3) temperature at constant reduction time and amount of reducing agent.

Dealing with the reduction of TiO_2 with ferrosilicon, for the purpose of rate calculation, the overall reduction reaction was assumed to be:



The reduction of TiO_2 can be considered to proceed in a series of small steps:

- (1) diffusion of reactants to interface;
- (2) reaction takes place on interface between slag melt and metal;

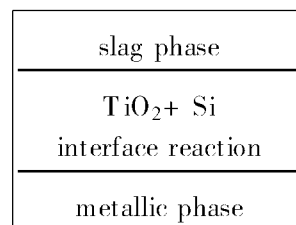


Fig. 1 The model devised for the silicothermic reduction of TiO_2

- (3) diffusion of reaction product into two phases.

For equation (1) the rate of silicothermic reduction of TiO_2 can be expressed as:

$$-dM_{\text{TiO}_2}/dt = -S \cdot dC(\text{TiO}_2)/dt$$

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$$= kA C(\text{TiO}_2)^a \cdot C(\text{Si})^b \quad (2)$$

where M_{TiO_2} is the mass of TiO_2 , g; S is the mass of slag which was assumed constant in all cases, g; $C(\text{TiO}_2)$ is the concentration of TiO_2 in the slag, %; $C(\text{Si})$ is the concentration of Si in ferrosilicon; A is the slag/ferrosilicon interfacial area, m^2 ; k is the rate constant; t is the reduction time, min.

Since the silicon concentration was constant, we have:

$$k' = kA C(\text{Si})^b \quad (3)$$

Equation (2) could be simplified to:

$$- dC(\text{TiO}_2)/dt = k' C(\text{TiO}_2)^a \quad (4)$$

$$- \frac{dC(\text{TiO}_2)}{C(\text{TiO}_2)^a} = k' dt \quad (5)$$

According to equation (1), $a = 1$, so:

$$- \frac{dC(\text{TiO}_2)}{C(\text{TiO}_2)} = k' dt \quad (6)$$

Integrating Eqn. (6) over $[C(\text{TiO}_2)_0, C(\text{TiO}_2)_t]$ and $[t_0, t]$

$$\int_{C(\text{TiO}_2)_0}^{C(\text{TiO}_2)_t} - \frac{dC(\text{TiO}_2)}{C(\text{TiO}_2)} = k' \int_{t_0}^t dt \quad (7)$$

where $C(\text{TiO}_2)_0$ is the initial concentration of TiO_2 ($t_0 = 0$); $C(\text{TiO}_2)$ is the concentration of TiO_2 after TiO_2 containing slag was reduced for t min.

$$C(\text{TiO}_2) = C(\text{TiO}_2)_0 e^{-k't} \quad (8)$$

According to the law of conservation of mass,

$$- dM_{\text{TiO}_2}/dt = - S \cdot dC(\text{TiO}_2)/dt \quad (9)$$

$$= k'' dM_{\text{Ti}}/dt = k'' W \cdot dC(\text{Ti})/dt$$

where W is the amount of reducing agent; k'' is a constant based on the relation of TiO_2 and Ti.

$$- S dC(\text{TiO}_2)/dt = W k'' dC(\text{Ti})/dt \quad (10)$$

$$- S dC(\text{TiO}_2) = W k'' dC(\text{Ti}) \quad (11)$$

$$- \int_{C(\text{TiO}_2)_0}^{C(\text{TiO}_2)_t} dC(\text{TiO}_2) = W k'' / S \cdot \int_{C(\text{Ti})_0}^{C(\text{Ti})_t} dC(\text{Ti}) \quad (12)$$

$$C(\text{TiO}_2) - C(\text{TiO}_2)_0 = - W k'' / S [C(\text{Ti})_0 - C(\text{Ti})] \quad (13)$$

When $t = 0$, $C(\text{Ti})_0 = 0$. Insert Eqn. (8) into Eqn. (13), we have:

$$C(\text{Ti}) = - S / k'' W \cdot C(\text{TiO}_2)_0 (1 - e^{-k't}) \quad (14)$$

According to Arrhenius,

$$k' = A e^{-E_a/RT} \quad (15)$$

where T is temperature; $R = 8.31$; E_a is activation energy.

3 EXPERIMENTAL

In the present study, the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag melt was investigated in the temperature range of 1500~1750 °C. The mixture of ferrosilicon, lime and TiO_2 containing slag was heated and maintained in the MoSi_2 heating furnace. The reactants were placed in a graphite crucible. The charge was made up of TiO_2 containing slag, lime and ferrosilicon in the stoichiometry proportion. The reaction products were sampled and analysed after the TiO_2 containing slag melt had been reduced for selected interval. Table 1 gives the details of the composition of materials used in the tests. The crushed size range of materials for the experiment was less than 1 mm.

Table 1 The chemical composition of materials(%)

Item	TiO ₂	CaO	Al ₂ O ₃	SiO ₂ or Si	MgO
TiO ₂ slag	23.5	27.3	13.85	24.3	8.22
CaO		98			
Ferro-Si				75.86	
Pure Si				98	

4 RESULTS AND DISCUSSION

The comprehensive test on the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag melt, which involved tests at various reduction times, was performed for the slag (described in Table 2). Similarly, the effect of temperature on the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag melt was determined for the slag.

4.1 Effect of Reduction Time on the Rate of TiO_2 Reduction

Experimental and calculated results are given in Table 2. In Fig. 2, comparisons are made

**Table 2 The experimental result of
silicothermic reduction of TiO₂
in TiO₂ containing slag melt**

No.	Charge/ g				<i>t</i> / min	<i>T</i> / °C	<i>C</i> (TiO ₂) / %
	Ferro -Si	Pure Si	TiO ₂ slag	CaO			
1	30		100	30	40	1600	6.17
2	30		100	30	50	1600	5.79
3	30		100	30	60	1600	5.58
4	30		100	30	70	1600	5.50
5	30		100	30	60	1500	7.98
6	30		100	30	60	1550	6.82
7	30		100	30	60	1650	3.94
8		30	100	30	60	1600	4.75

The effect of reduction temperature on the rate of TiO₂ reduction was investigated in the temperature range of 1 550 ~ 1 780 °C. Fig. 4 gives the reaction temperature versus the rate of TiO₂ reduction. The rate of TiO₂ reduction increased with increasing reaction temperature.

**Fig. 3 Effect of reaction time on
the concentration of TiO₂**

**Fig. 2 Effect of reduction time on
the rate of TiO₂ reduction**

between the results of experimental data and the above mentioned mathematic model, showing that the mathematic model agrees satisfactorily with experimental results. It was found that the retardation of the rate of silicothermic reduction of TiO₂ in TiO₂ containing slag melt took place in the reduction process, which was attributed to the decrease of TiO₂ content of TiO₂containing slag melt. During the reduction process, TiO₂ in the slag melt was reduced to titanium silicide and then transferred to the metallic phase; secondary SiO₂ product was produced and entered into the slag phase. It was no use prolonging the reduction time since very little TiO₂ was reduced after 60 min, i. e. , an equilibrium was attained.

4. 2 *Effect of Reduction Temperature
on the Rate of TiO₂ Reduction*

**Fig. 4 Effect of reduction temperature
on the rate of TiO₂ reduction**

4. 3 *Effect of the Amount of Reducing
Agent on the Rate of TiO₂ Reduc-
tion*

Table 2 shows the effect of the amount of reducing agent on the rate of TiO₂ reduction. The results indicated that the rate of TiO₂ reduction increased with increasing reaction temperature.

4. 4 *Effect of the Amount of Reducing
Agent on the Rate of TiO₂ Reduc-
tion*

Table 2 shows the effect of the amount of the reducing agent on the rate of TiO_2 reduction. The results indicated that the rate of TiO_2 reduction increased with increasing amount of reducing agent. According to Eqn. (2), $C(\text{Si})$ is the factor that influenced the rate of TiO_2 reduction.

5 CONCLUSIONS

(1) The decrease of the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag melt takes place throughout the reduction process. It is no use prolonging the reduction time since very little TiO_2 will be reduced after 60 min.

(2) For an initial TiO_2 content of 23.5 percent, the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag increases with increasing

reduction temperature.

(3) An increase in the TiO_2 content in TiO_2 containing slag generally causes an increase in the rate of reduction of TiO_2 .

(4) The amount of reducing agent is a factor that accelerates the rate of silicothermic reduction of TiO_2 in TiO_2 containing slag melt.

(5) The kinetic parameters of the silicothermic reduction of TiO_2 in TiO_2 containing slag melt are given by $C(\text{TiO}_2) = C(\text{TiO}_2)_0 e^{-k't}$, where $C(\text{TiO}_2)_0 = 23.5\%$, $k' = 0.025$.

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electroreduction of Cu^{2+} to Cu is reversible with two steps.

For the reversible charge transfer with soluble product, the relation of peak current and sweep rate is as follows^[6(d)]:

$$I_p = 0.4463(nF)^{3/2}(Dv/RT)^{1/2}AC \quad (6)$$

From the slope of line in Fig. 6(b) and the equation (6), the D of Cu^{2+} was calculated as $1.27 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ (125 °C).

4 CONCLUSIONS

(1) The electroreduction of Zn^{2+} , Ni^{2+} and Cu^{2+} has different kinetic characters. The charge transfer of Zn^{2+} is reversible in one step. The charge transfer of Ni^{2+} is irreversible in one step. The charge transfer of Cu^{2+} is reversible with two steps.

(2) The diffusion coefficients of Zn^{2+} , Ni^{2+} and Cu^{2+} in urea-metal chlorides melt were

determined. The order of magnitude of D is $10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ (125 °C).

(3) The transfer coefficient α of electrode reaction: $\text{Ni}^{2+} + 2e = \text{Ni}$ was determined as 0.47.

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