COUPLING PROCESS FOR Ti AND Si BETWEEN TITANIA SLAGS AND Cu MELTS AT 1 500 ℃①

Xue, Xiangxin Che, Yinchang
Department of Ferrous Metallurgy, Northeastern University, Shenyang 110006

ABSTRACT An experimental study of the mass transfer of Ti and Si between slags containing TiO_2 and Cu-Ti-Si melts under constant oxygen pressure at 1 500 ℃ has been made. Apparent mass transfer coefficients of Ti and Si in Cu-Ti-Si melts were obtained and coupling process transfer of both Ti and Si was discussed.

Key words: coupling reaction apparent mass transfer coefficient titania slag Cu melt

1 INTRODUCTION

Understanding of coupling process for Ti and Si between titania slags and Cu-Ti-Si melts is essential for studying the preparation of Cu alloys. Though Mori *et al*[1] studied the oxidizing process of Si in Cu melt coexisting with Li_2O-SiO_2-Al_2O_3-FeO slag and gave an apparent mass transfer coefficient of Si in the melt, so far no publication for the Cu-Ti-Si melt was available. The present paper studied experimentally the oxidizing processes of Ti and Si in the Cu-Ti-Si melts at 1 500 ℃ and constant oxygen pressure, estimated the apparent mass transfer coefficients, and discussed the coupling process of both Ti and Si between titania slags and Cu melts at 1500 ℃.

2 EXPERIMENTAL

A master alloy of Cu-Ti-Si was prepared using electrolytic Cu (> 99. 99 wt.-%), Ti powder(>99. 95 wt.-%) and single crystal Si (>99. 999 wt.-%) in a vacuum non-consumable electrode furnace. A master slag was made by use of analytically pure reagent of TiO_2, SiO_2 and so on. A Mo cylinder with mean diameter of 14. 00 mm and thickness of 0. 1~0. 2 mm was made and inserted into the Al_2O_3 crucible to prevent slag leaking. An alloy bath at high temperature under argon atmosphere in the crucible was prepared before every experimental run, and preparing conditions(Ar rate of flow, temperature programm and constant time) of each were the same as others. The bath was covered with Mo plate and scrap of sponge Ti to prevent oxidation of Ti and Si. The alloy bath was taken out of the furnace when its temperature was up to 300 ℃ under argon atmosphere deoxidized by magnesium scrap.

Oxygen pressure controlling system was similar to that in Ref. [2] and [3]. Ratios of $H_2O/H_2=2.50\times10^{-3}$ and $Ar/H_2=4\sim5$ in gas mixture were held constant to prevent thermodiffusion. Obtained p_{H_2O} in the mixture was agreement with that in Ref. [2] and [3].

Vacuum-pumping and argon purging were carried out repeatedly after putting the samples into the furnace. Then the samples were program-heated and held at a constant temperature of 1 500 ℃ under argon atmosphere deoxidized by magnesium scrap. Purified hydrogen was introduced into the furnace at 1 200 ℃. After the temperture being constant at 1 500 ℃, moisture was carried by hydrogen into the furnace. From then on reaction time was recorded. The samples and their concentrations at this time were considered as initial ones. At the end of experiment the

---

① Received Jan. 24, 1994; accepted in revised form Nov. 15, 1994

H_2O/H_2 gas mixture was cut off and residual mixture was exhausted by argon for 20 min, and then the crucibles were taken out and quenched promptly in water. Set-time sampling was used to prevent from getting out of control on the atmosphere. The experimental furnace and crucible assembly used in the experimental runs are shown in Fig. 1.

A furnace with heating elements of $MoSi_2$ and a programming controller of SJK-1800 type were used in the experiments. The temperature was controlled within ±2 ℃ at 1 513 ℃ for a working zone of 60 mm in height.

The temperature was measured by a calibrated PtRh6-PtRh30 thermocouple in connection with a precise potentiometer. The system was air-tight through out the experimental runs.

3 RESULTS

Three slags containing TiO_2 and SiO_2 were made in coexistence with three Cu-Ti-Si melts of different initial concentrations. Results at different time are shown in Fig. 2. All time dependences of $\lg[Si]_{Cu}$ have inflexion points at a time of 1.0h, and each of them can be expressed as a linear equation. It is believed that reaction $[Si]_{Cu} + [O]_{Cu} = (SiO_2)$

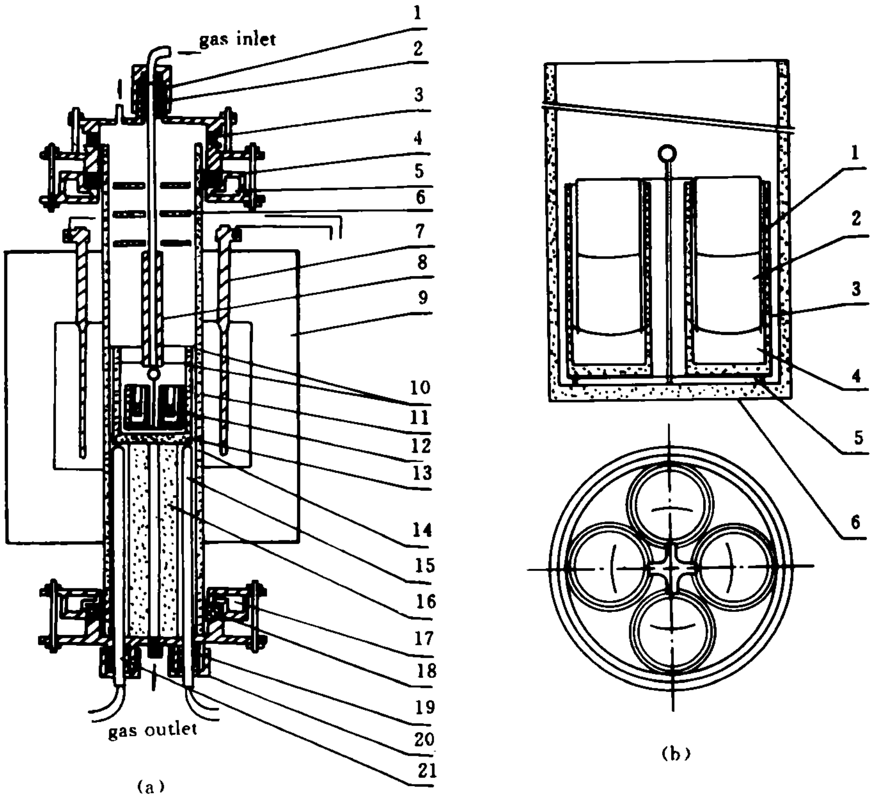

Fig. 1 Experimental furnace(a) and crucible assembly(b)

(a): 1, 20—gland nut; 2, 3, 4, 18, 19—sealing rubber washers; 5, 17—sleeve for cooling water; 6—shields; 7—$MoSi_2$ heater; 8—lance; 9—refractory; 10—Mo covers; 11—Al_2O_3 tube; 12, 13—Al_2O_3 crucible; 14—Mo tray; 15, 21—protection tubes for thermocouples; 16—crucible supportor;

(b): 1—Mo cylinder; 2—molten slag; 3—Al_2O_3 crucible; 4—Cu melt; 5—Mo tray; 6—Al_2O_3 crucible proceeds very fast[1]. In accordance with the fact that the oxidation of Ti is easier than Si[4], it is also believed that chemical reactions (1) and (1′) proceed very fast at the elevated temperature.

$$[\mathrm{Ti}]_{\mathrm{Cu}}+2\mathrm{H_2O}=(\mathrm{TiO_2})+2\mathrm{H_2} \qquad (1)$$

$$[\mathrm{Si}]_{\mathrm{Cu}}+2\mathrm{H_2O}=(\mathrm{SiO_2})+2\mathrm{H_2} \qquad (1')$$

Thus, it is acceptable to suggest that the mass transfer of Ti and Si in Cu-Ti-Si melts is the control step in the reactions, and the rate of apparent mass transfer process can be expressed as follows:

$$-\mathrm{d}n_j/\mathrm{d}t = k_j A(C_j - C_{j,i}) \qquad (2)$$

where $-\mathrm{d}n_j/\mathrm{d}t$ is change in mole for component j in Cu-Ti-Si melts in unit time; k_j is apparent mass transfer coefficient of j; C_j and $C_{j,i}$ are instant and interface concentration of j respectively; A is reaction area and i represents interface. At the beginning of the reaction, $C_{j,i} \ll C_j$, so $C_{j,i}$ can be omitted from rate equation and then the Eq. (2) can be simplified as follows:

$$-\mathrm{d}n_j/\mathrm{d}t = k_j A C_j \qquad (3)$$

Intergratting Eq. (3) with respect to time, Eq. (4) can be obtained:

$$-\lg[j]/[j]_0 = k_j' A t/V_m \qquad (4)$$

where V_m is volume of the Cu-Ti-Si melt; j represents Ti and Si respectively. It is obvious that Eq. (4) is a linear function. Comparing with regression equations obtained from the experimental runs, the slop T of regression equations in Fig. 2 must be equal to Ak_j'/V_m, where A and V_m are estimated from a mean value for five measurements of semi-sphere reaction interface and volume of the melts, and A is $2.70\mathrm{cm}^2$, V_m $0.84\mathrm{cm}^3$. Then k_j' is calculated from $T = 3.21 k_j'$ and given in Table 1. It can be seen that k_{Ti}' is larger than k_{Si}' and that k_{Ti}' will be decreased by one order of magnitude when Si is added into Cu-Ti melts.

4 DISCUSSION

It is possible to change the ordinate, $\lg[j]$ in Fig. 2, into $\lg[j]/[j]_0$, and make a plot of $\lg[\mathrm{Ti}]/[\mathrm{Ti}]_0$ against $\lg[\mathrm{Si}]/[\mathrm{Si}]_0$ as shown in Fig. 3. It can be seen that relations between $\lg[\mathrm{Ti}]/[\mathrm{Ti}]_0$ and $\lg[\mathrm{Si}]/[\mathrm{Si}]_0$ are linear expressions and vice versa. For Ti and Si in Cu melts, Eq. (5) and (5′) are obtained from Eq. (4):

$$-\lg[\mathrm{Ti}]/[\mathrm{Ti}]_0 = k'_{\mathrm{Ti}} A\, t/V_m \qquad (5)$$

$$-\lg[\mathrm{Si}]/[\mathrm{Si}]_0 = k'_{\mathrm{Si}} A\, t/V_m \qquad (5')$$

where A/V_m of the equations are the same in the experimental conditions. The Eq. (5) is divided by Eq. (5′) and then Eq. (6) is given as follows:

$$\lg[\mathrm{Ti}]/[\mathrm{Ti}]_0/\lg[\mathrm{Si}]/[\mathrm{Si}]_0 = k'_{\mathrm{Ti}}/k'_{\mathrm{Si}} = C \qquad (6)$$

where C is a constant. It is obvious that Eq. (6) is mathematically similar to the regression equations in Fig. 3. Comparing it with equations in Fig. 3, the C in equation is the slop T' of regression equation, and results are given in Table 2.

According to Eq. (4), both ordinate and abscissa in Fig. 3 are a function of time, but all regression equations have not time variables because of plotting at iso-time condition,

Table 1 Initial concentration and apparent mass transfer coefficient

Slag initial concentration (wt.-%)					Cu melt (wt.-%)		Apparent mass transfer coefficient/cm·h^{-1}	
CaO	SiO	Al_2O_3	MgO	TiO_2	C_{Si}^0	C_{Ti}^0	k_{Si}'	k_{Ti}'
	94.00			6.00	5.96	4.01	1.25×10^{-2}	3.34×10^{-2}
							3.12×10^{-2}	9.35×10^{-2}
25.00	28.00	11.00		35.00	5.65	3.02	1.25×10^{-2}	6.85×10^{-2}
							3.12×10^{-2}	
23.00	25.10	10.90	5.10	35.00	5.82	2.66	3.12×10^{-3}	4.67×10^{-2}
							1.56×10^{-2}	
TiO_2 after Ref. [5]						0.91		1.60×10^{-1}

Table 2 Ratio of relative apparent mass transfer coefficients

Slag system(wt. -%)					k'_{Ti}/k'_{Si}		
CaO	SiO_2	Al_2O_3	MgO	TiO_2	1	2	
	94.00			6.00	2.85		Fig. 3
					2.74	3.00	Tab. 1
25.00	28.00	11.00		35.00	5.35	14.70	Fig. 3
					5.48	20.77	Tab. 1
23.00	25.10	10.90	5.10	35.00	15.08	2.50	Fig. 3
					14.97	2.99	Tab. 1

which can be explained as that the time is out of function for relative mass transfer when mass transfer process of Ti is simultaneous with that of Si, or k'_{Ti}/k'_{Si} is a constant, and vice versa ($k'_{Si}/k'_{Ti} = 1/C$). The meaning of k'_{Ti}/k'_{Si} is a ratio of relative apparent mass transfer for Ti vs Si when both Ti and Si transfer occur simultaneously at iso-time condition. It can be expressed as a coupling effect for the two processes.

A relative apparent diffusion ratio D'_{Ti}/D'_{Si}, a constant, can be obtained from $k'_{Ti}/k'_{Si} = C$, because it is a dimensionless number and $k'_{Ti}/k'_{Si} = D'_{Ti}/D'_{Si} = C$, which can be considered as the phenomena of identity between mass transfer and diffusion for Ti and Si when a coupling effect occurs at iso-time condition.

All apparent mass transfer coefficients of Ti, k'_{Ti} were divided by k'_{Si} in Table 1, and results are given as shown in Table 2. Comparing the data of k'_{Ti}/k'_{Si} from equation (6) with that from Table 1, it can be seen that both k'_{Ti}/k'_{Si} are agreeable and order of magnitude is the same. In all cases the values of k'_{Ti}/k'_{Si} are larger than unity, or k'_{Ti} larger than k'_{Si} in Table 2, which can be explained, on the one hand, by the fact that the affinity of Ti for oxygen dissolved in Cu-Ti-Si melt is larger than that of Si. Hence, the oxidation of Si is limited by that of Ti, which might result in the increment of transfer resistance for Si. On the other hand, for lack of oxygen in reaction zone, the limited oxygen could only react with titanium in the melts and the oxidation rate of Si was reduced, it is possible to cause that the values of k'_{Ti} are larger than that of k'_{Si} in Table 2. In addition, the coupling effect between chemical reaction and transfer processes must cause response of apparent mass transfer of Si although the initial concentration of Ti is less than that of Si.

Comparing the data given in Table 1 with

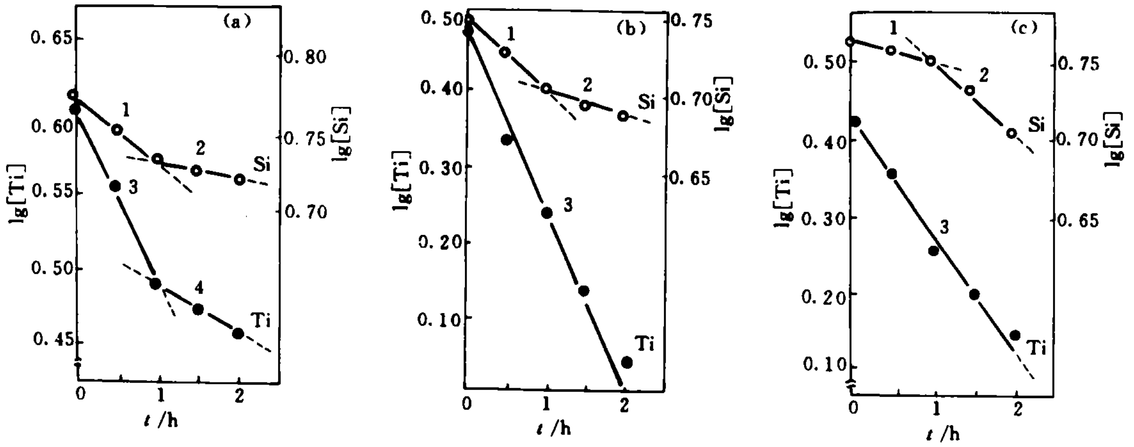

Fig. 2 Time dependence of lg[Si] and lg[Ti]

(a)—TiO_2-SiO_2;
1——$lg[Si]=0.78-0.04t$;
2——$lg[Si]=0.75-0.01t$;
3——$lg[Ti]=0.61-0.11t$;
4——$lg[Ti]=0.53-0.03t$

(b)—CaO-SiO_2-Al_2O_3-TiO_2;
1——$lg[Si]=0.75-0.04t$;
2——$lg[Si]=0.72-0.01t$;
3——$lg[Ti]=0.47-0.22t$

(c)—CaO-SiO_2-Al_2O_3-MgO-TiO_2
1——$lg[Si]=0.77-0.01t$;
2——$lg[Si]=0.80-0.05t$;
3——$lg[Ti]=0.43-0.15t$

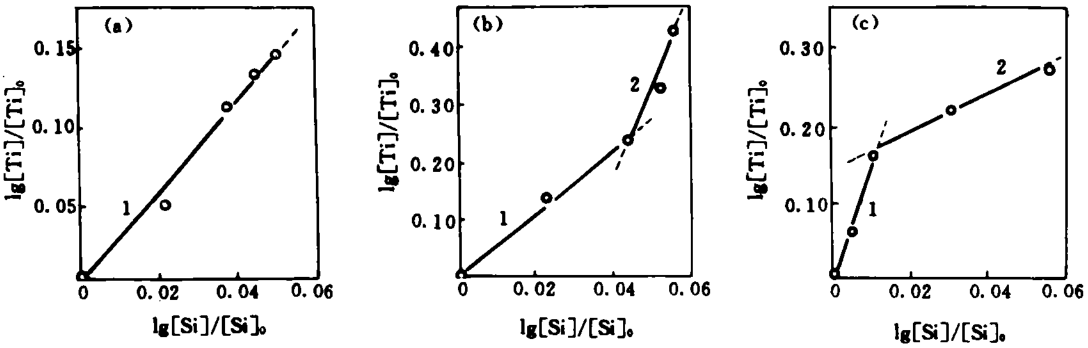

Fig. 3 **$\lg[Ti]/[Ti]_0$ vs $\lg[Si]/[Si]_0$ in different slags at** 1 550 ℃

(a)TiO_2-SiO_2

1——$\lg[Ti]/[Ti]_0 = 2.85 \lg[Si]/[Si]_0$;

(b)CaO-SiO_2-Al_2O_3-TiO_2

1——$\lg[Ti]/[Ti]_0 = 5.35 \lg[Si]/[Si]_0$; 2——$\lg[Ti]/[Ti]_0 = -0.41 + 14.70 \lg[Si]/[Si]_0$;

(c)CaO-SiO_2-Al_2O_3-MgO-TiO_2

1——$\lg[Ti]/[Ti]_0 = 15.08 \lg[Si]/[Si]_0$; 2——$\lg[Ti]/[Ti]_0 = 0.02 + 2.50 \lg[Si]/[Si]_0$

Ref[5], it can be seen that k'_{Ti} is lowered by one order of magnitude after the addition of Si into Cu-Ti melts, which suggests that transfer path is much crowded and apparent mass transfer of Ti is affected by the addition of Si.

It seems that the inflexion points for the time dependence of $\lg[Si]$ at 1.0 h in Fig. 2, which results in that the same inflexion points for $\lg[Si]/[Si]_0$ dependence of $\lg[Ti]/[Ti]_0$, are attributed to the Ti and Si transfer processes with initial rate difference before 1.0h, and after 1.0 h new rate difference arise from the coupling effect of transfer processes for Ti and Si, so there have been the inflexion points in Fig. 2 and Fig. 3. The apparent mass transfer coefficients of Ti and Si in Cu-Ti-Si melts coexisting with different slags were obtained from experimental results at constant oxygen pressure and static state(non-stirring). There have not been any similar reports given yet. An apparent mass transfer coefficient of Si in molten Cu coexisting with Li_2O-SiO_2-Al_2O_3-FeO slags under stirring condition was given in Ref. [1]. The k'_{Si} in Ref. [1] is larger than k'_{Si} obtained in present work by three order of magnitude. This disagreement might be caused by different experimental conditions, especially stirring.

5 CONCLUSION

An experimental study has been made of the apparent mass transfer and coupling process for Ti and Si between slags containing TiO_2 and Cu-Ti-Si melts under constant oxygen pressure at 1 500 ℃. Apparent mass transfer coefficients of Ti and Si in Cu-Ti-Si melts were obtained. The relative apparent mass transfer, k'_{Ti}/k'_{Si}, was estimated.

REFERENCES

1 Mori, K *et al.* Tetsu-to-Hagane, 1985, 71: 1110.

2 Baxter, G P; Lansing, J E. J Amer Chem Soc, 1920, 42: 419.

3 Zhou, J C *et al.* In: Symposium of the Excellent Papers for Chinese Society of Metals in 1979-1980. Beijing: Metallurgic Industry Press, 1984.

4 Xue, X X *et al.* Eng Chem Metall, 1989, 3: 64.

5 Xue, X X *et al.* Acta Metall Sin, 1990, 26B: 140.