Vol. 11 № 4 **Trans. Nonferrous Met. Soc. China** Aug. 2001

[Article ID] 1003- 6326(2001)04- 0535- 05

Experimental thermodynamic research on equilibrium between silicon alloy and SiO_2-CaO-Al_2O_3 melt①

WANG Xin-guo(王新国), DING Wei-zhong(丁伟中), TANG Kai(唐 恺),
JIANG Guo-chang(蒋国昌), XU Kuang-di(徐匡迪)
(Shanghai Enhanced Laboratory of Ferrometallurgy, Shanghai University,
Shanghai 200072, P. R. China)

[Abstract] The equilibria of Al and Ca between silicon alloy and the SiO_2-Al_2O_3-CaO ternary slags were investigated using graphite crucible at 1 550 ℃. With increasing Al_2O_3 and CaO content in the slags, the Al and Ca content increase respectively. The variation of the impurities are also affected by the silica content in slag which provides the oxidant during the oxidation refining process. The distributions of the impurities Al and Ca in silicon were given in terms of isoconcentration curves for Al and Ca in the ternary slags of SiO_2-Al_2O_3-CaO. The present experimental work provided available data to analyze the action of Al and Ca during oxidation refining process for silicon alloy.

[Key words] silicon; oxidation refining; thermodynamic equilibrium

[CLC number] TG 146 **[Document code]** A

1 INTRODUCTION

Metallurgical grade silicon (MG-Si) is produced in arc furnace by reducing the silicon oxide with carbon. Both the silicon oxide and carbon are not purer than expected, there are about 1 to 2 percent impurities such as aluminium, calcium, phosphor and iron existing in the products[1]. Usually the MG-Si acts as the starting material for the chemical silicon, solar grade silicon (SOG-Si) and semiconductor grade silicon (SEG-Si), the impurities are harmful to the use. Therefore, the methods of purification or prepurification have been explored recently. The techniques mainly include three types. One way is the acid leaching process[2~6] in hydrometallurgy, which uses different acids of HCl, H_2SO_4, aqua regia etc to deal with the pulverized silicon. The acid leaching process is always used in the production of high purity silicon, such as SOG-Si or SEG-Si. It is seldom used in the prepurification of MG-Si because of its treatment efficiency. The second way is the purification with chlorine gas, which makes the impurities of Al, Ca into gaseous chlorides[2,7]. It is prohibited because of the pollution aspects.

Oxidation refining process acts as another way to purify the MG-Si, in which elements with higher oxygen affinity than silicon are converted to their oxides forming a silicate slag[7~9]. The oxidant is usually provided by oxygen, solid silica or synthetic silicate slags. It has been found that the calcium and aluminium can be decreased through the oxidation refining process. Many factories have purified the MG-Si by this method efficiently since it causes less pollution to the surroundings than any other methods. Though many researchers[7,9,10] have reported the thermodynamic properties of the Si-base alloys, the systematic equilibrium data between the silicon alloy and the silicate slags are still unclear.

We performed the equilibrium measurements on the distribution of calcium, aluminium between liquid silicon and slags in the entire liquid phase.

2 OUTLINE OF OXIDATION REFINING METHOD

The oxidation refining process can be carried out by oxygen or silicate slags. We take the Si-Al-Ca-O system into consideration. So the ternary alloy Si-Al-Ca will be in equilibrium with the slag system of SiO_2-Al_2O_3-CaO during the oxidation refining process. By the phase rule, the degree of freedom during the refining process is two at a given temperature and pressure. The reactions used to identify the ultimate equilibrium state are the following,

$$\frac{3}{4}(\mathrm{SiO_2}) + [\mathrm{Al}] = \frac{1}{2}(\mathrm{Al_2O_3}) + \frac{3}{4}[\mathrm{Si}]$$

$$x_{[\mathrm{Al}]} = \frac{1}{K_{\mathrm{Al}}} \cdot \frac{a_{[\mathrm{Si}]}^{3/4}}{\gamma_{[\mathrm{Al}]}} \cdot \frac{a_{(\mathrm{Al_2O_3})}^{1/2}}{a_{(\mathrm{SiO_2})}^{3/4}} \tag{1}$$

$$\frac{1}{2}(\mathrm{SiO_2}) + [\mathrm{Ca}] = (\mathrm{CaO}) + \frac{1}{2}[\mathrm{Si}]$$

$$x_{[\mathrm{Ca}]} = \frac{1}{K_{\mathrm{Ca}}} \cdot \frac{a_{[\mathrm{Si}]}^{1/2}}{\gamma_{[\mathrm{Ca}]}} \cdot \frac{a_{(\mathrm{CaO})}}{a_{(\mathrm{SiO_2})}^{1/2}} \tag{2}$$

---

① **[Foundation item]** Project (97XD14005) supported by the Natural Science Foundation of Shanghai

[Received date] 2000- 07- 26; **[Accepted date]** 2001- 02- 19

The parentheses indicate the slag phase and the brackets, the silicon phase.

At given temperature, a_{Si}, $\gamma_{\mathrm{Al}}^{\mathrm{Si}}$, $\gamma_{\mathrm{Ca}}^{\mathrm{Si}}$ are constant[7]. Then from Eqns. (1) and (2), we know that the equilibrium impurities of Al and Ca are the functions of activity ratios of $a_{(\mathrm{Al_2O_3})}^{1/2}/a_{(\mathrm{SiO_2})}^{3/4}$ and $a_{(\mathrm{CaO})}/a_{(\mathrm{SiO_2})}^{1/2}$. There must exist a series of points in the slag liquidus where the ratios of $a_{(\mathrm{Al_2O_3})}^{1/2}/a_{(\mathrm{SiO_2})}^{3/4}$ and $a_{(\mathrm{CaO})}/a_{(\mathrm{SiO_2})}^{1/2}$ are constant respectively, which represents the same equilibrium concentrations of Al and Ca in the silicon. Therefore, the equilibrium concentrations of impurities can be expressed by the iso-concentration curves of $w(\mathrm{Al})$ and $w(\mathrm{Ca})$ in the slag phase diagrams. Schei et al[7] has given such diagram (Fig. 1) with the activities in $\mathrm{SiO_2}$-$\mathrm{Al_2O_3}$-CaO slag calculated by Rein et al[11] and the thermodynamics properties of the silicon alloy measured by Weiss et al[9], Ottem[12] and Margaria[13], in which the activity coefficients of the impurities in silicon are $\gamma_{\mathrm{Al}}^{\mathrm{Si}} = 0.38$, $\gamma_{\mathrm{Ca}}^{\mathrm{Si}} = 5.2 \times 10^{-4}$ respectively at 1 550 ℃.

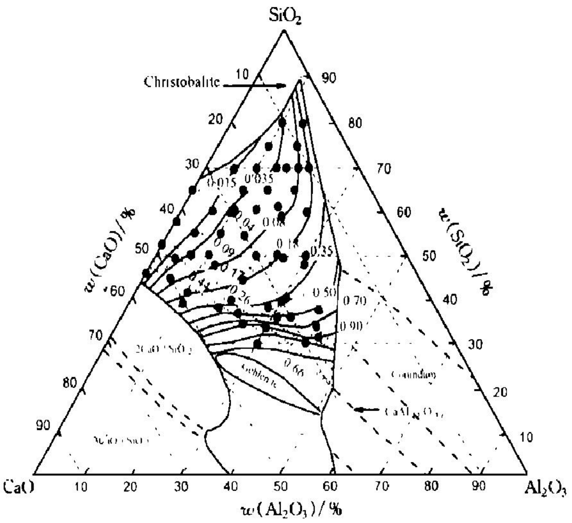

Fig. 1 Compositions of $\mathrm{SiO_2}$-$\mathrm{Al_2O_3}$-CaO slags in equilibrium with silicon alloy

In our present study, the selection of initial slag and silicon compositions are based on the iso-concentration curves calculated by Schei et al[7], which are expressed by the solid circle points in Fig. 1.

The chemicals used in the present study are listed in Table 1. Master slags were premelted in graphite crucibles. The quenched slags were crushed to small grains for use in the following experiments. The prepared master slags were analyzed to reconfirm their chemical composition. Pure oxides were always used to adjust the compositions of the slags. The alloys were prepared with the MG-Si, crystal silicon and pure aluminium powder.

The experiments were carried out at 1 550 ℃ with the slag/metal ratio of 1.5~ 2.0.

Table 1 Quality of chemicals used in experiment

Compounds	Quality
$\mathrm{SiO_2}$(powder)	Analytical grade
$\mathrm{Al_2O_3}$(powder)	Analytical grade
$\mathrm{CaCO_3}$(powder)	> 99.0%
MG-Si (lump)	Al: 0.125 8%, Ca: 0.621 6%
Crystal Si (lump)	> 99.999 9%
Al (powder)	> 99.99%
Ar (gas)	> 99.99%

3 EXPERIMENTAL

The experimental apparatus for the equilibrium measurements is shown schematically in Fig. 2. The electric furnace was powered with graphite heater. The temperature was kept constant within ±2 ℃ by a controller which was activated by a Pt/Pt-10% Rh thermocouple-1 located outside of the graphite heater. The actual temperature of the sample was measured by another thermocouple-2 placed under the crucible a few milimeters away.

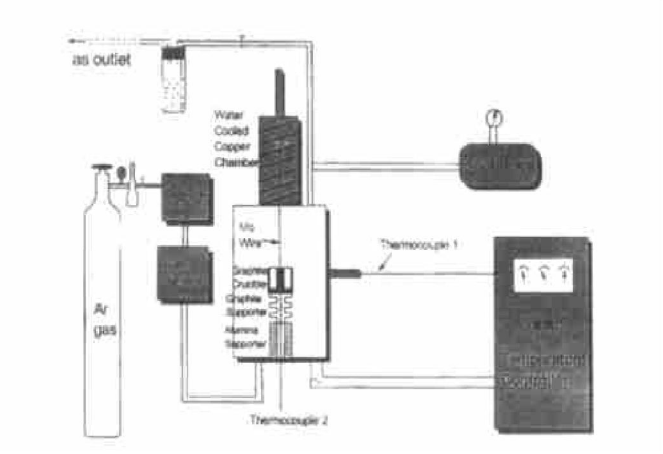

Fig. 2 Experimental apparatus for equilibrium measurements

The furnace was evacuated to a certain degree at beginning and then flushed with argon gas with purity of 99.994%. The argon gas was purified with Mg slices (200 ℃) and drying agent for oxygen and water removal before passing through the furnace. The whole experiment process proceeded under the argon atmosphere to avoid the oxidation of the graphite material.

The crucible (45 mm O. D. and height) was made of high-purity graphite. All of the crucibles are of four holes type, each hole (12 mm I. D. and 40 mm height) acts as a separate container.

The crucible, charged with appropriate amounts of slag and silicon alloy with desired compositions, was lowered into the reaction zone of the furnace. The system was then sealed and evacuated two times with intermediate of Ar gas. The crucible was heated from room temperature to the desired temperature

1 550 ℃ in about 2 h. The necessary time to reach the slag/metal equilibrium was 4 h, which was determined in preliminary experiments. After equilibration, the crucible was rapidly lifted to the water cooled copper tube above the furnace by a Mo wire.

The samples of slag and silicon alloy were separated carefully and crushed by carnelian mortar respectively. The atomic emission spectroscopy ICP method was used to analyze the chemical compositions.

4 RESULTS AND DISCUSSION

The equilibrium data of the experiments are listed in Table 2.

4.1 Relations of compositions between silicon and slag

With increasing alumina content of the slag, the aluminium content in the silicon increases as expected. The data are illustrated in Fig. 3. The experimental data of Weiss[9] are also added to Fig. 3, in which the equilibrium concentrations of aluminium and calcium in silcon were measured along the silica saturation line in SiO_2-Al_2O_3-CaO system.

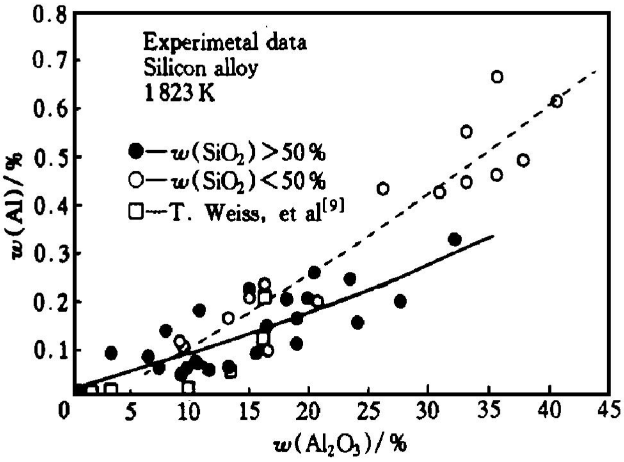

Fig. 3 Relations between Al content in silicon and Al_2O_3 content in slag at 1 550 ℃

From Eqn. (1), we know that the equilibrium aluminium content in silicon alloy attaches closely to the properties of the alloy and the slag. The activity coefficient of aluminium γ_{Al}^{Si} in infinite dilute Si-based solution can be treated only as the function of temperature[9]. The silicon acts as nearly the pure matter, so its activity is about the constant of unit.

Consequently, the equilibrium content of aluminium in silicon is directly controlled by the activities of silica and alumina in slag at fixed temperature.

The isoactivity curves of alumina in SiO_2-Al_2O_3-CaO at 1 550 ℃ was given by Rein et al[11], Kay et al[14] and Ohta et al[15] in Fig. 4. In the liquid phase of slag, the value of $a_{Al_2O_3}$ increases with increasing alumina content in the slag if the silica content is fixed, which leads to the increase of the Al content in the silicon alloy.

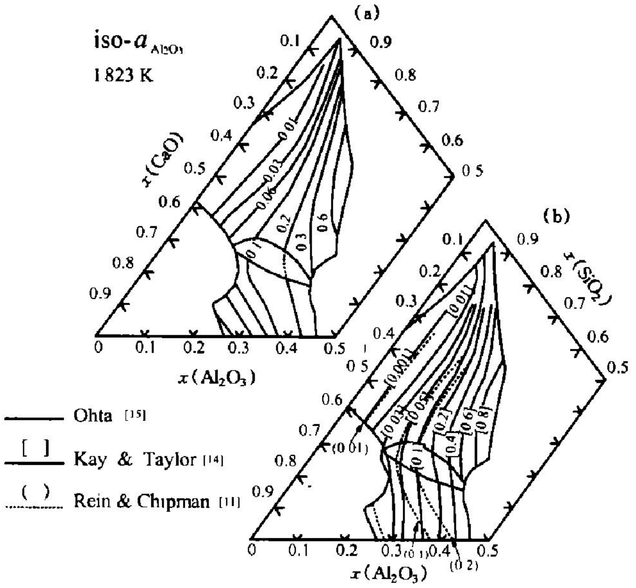

Fig. 4 Isoactivity curves of alumina in slags of SiO_2-Al_2O_3-CaO at 1 550 ℃[11, 14, 15]

Another information is expressed from Fig. 4, where the isoactivity curves of alumina distribute more compact when the silica content $x(SiO_2) > 0.45$ (or > 50% (mass fraction)). In other words, the little variation of the alumina content will cause biggish change of $a_{Al_2O_3}$. The aluminium content in equilibrium with the slag in such region will sure change successively following the change of slag compositions, the solid circle points show such trends in Fig. 3. While the silica content $x(SiO_2) < 0.45$ (or < 50% (mass fraction)), the change of $a_{Al_2O_3}$ is less sensitive to the variation of the alumina content in slags, and the isoactivity curves of alumina disperse. Simultaneously, the activities of silica decrease since the silica content is low, which means that the oxidation ability of the slags lowers. So the equilibrium aluminium content in the silicon alloy increases and the equilibrium data scatter. The above analysis is proved by the experiment data listed in Table 2 and Fig. 3. The data agree well with those of Weiss[9] who examined the equilibrium aluminium content in silicon alloy with the silica-rich slag.

The same explanation to the equilibrium calcium content can be also obtained from the activities of the silicon alloy and the CaO in slag. The relationship between the calcium content in silicon and the CaO content in slag is schemed in Fig. 5.

4.2 Distribution of aluminium and calcium in equilibrium with slags

Fig. 6 and Fig. 7 show the distributions of the

Table 2 Results obtained in equilibration of silicon with slags in graphite crucibles at 1 550 ℃ (mass fraction, %)

No.	Slag/metal	Slags			Silicon alloy	
		SiO_2	CaO	Al_2O_3	Al	Ca
1	1.5	76.80	12.50	10.70	0.0745	0.0184
2	1.5	55.71	35.77	8.52	0.0676	0.0374
3	1.5	34.33	25.81	40.86	0.6118	0.0944
4	1.5	67.79	22.94	9.27	0.0206	0.0362
5	1.5	81.37	7.65	10.98	0.1795	0.0082
6	1.5	76.76	15.28	7.96	0.1361	0.0653
7	1.5	71.36	9.63	19.01	0.1077	0.0307
8	1.5	52.41	15.36	32.23	0.3246	0.0403
9	1.5	57.44	12.99	27.72	0.1965	0.0437
10	1.5	49.87	19.02	31.11	0.4226	0.0376
11	1.5	49.32	41.03	9.65	0.1029	0.0715
12	1.5	48.70	30.48	20.82	0.1976	0.0652
13	1.5	59.96	30.23	9.81	0.0607	0.0514
14	1.5	47.45	37.39	15.16	0.2068	0.2755
15	1.5	64.47	15.03	20.50	0.2559	0.0436
16	1.5	60.52	21.35	18.13	0.2012	0.0431
17	1.5	51.15	24.72	24.13	0.1547	0.0228
18	2.0	54.64	45.06	0.30	0.0122	0.1300
19	2.0	74.17	25.63	0.20	0.1585	0.2218
20	2.0	62.79	36.51	0.69	0.0148	0.0689
21	2.0	65.75	34.02	0.23	0.0139	0.1316
22	2.0	34.59	27.24	38.17	0.4914	0.4544
23	2.0	42.66	23.96	33.38	0.4461	0.1397
24	2.0	31.98	42.31	25.71	0.6035	0.2940
25	2.0	38.01	35.70	26.29	0.4317	0.3687
26	2.0	33.33	30.66	36.01	0.6654	0.2612
27	2.0	38.50	25.54	35.96	0.4586	0.1866
28	2.0	37.02	29.60	33.38	0.5512	0.1428
29	2.0	34.91	37.59	25.50	0.6121	0.1324
30	2.0	34.71	41.84	23.45	0.7693	0.3368
31	2.0	40.10	43.54	16.45	0.2345	0.2551
32	2.0	47.98	24.50	27.52	0.1027	0.0644
33	2.0	40.55	21.32	38.13	0.2849	0.1017
34	2.0	46.64	36.60	16.76	0.0951	0.0984
35	2.0	45.46	45.25	9.29	0.1148	0.2126
36	2.0	81.85	7.49	10.66	0.0732	0.1141
37	2.0	71.80	12.61	15.59	0.0914	0.0086
38	2.0	61.94	18.25	19.81	0.2033	0.0220
39	2.0	48.12	38.58	13.30	0.1631	0.1201
40	2.0	60.45	18.08	21.47	0.0894	0.0158
41	2.0	51.74	24.79	23.46	0.2437	0.0229
42	2.0	63.50	27.16	9.34	0.048	0.0681
43	2.0	54.71	32.46	7.43	0.060	0.0510
44	2.0	74.08	16.91	9.01	0.7858	0.0403
45	2.0	60.10	32.81	7.09	0.2018	0.0105
46	2.0	59.35	37.22	3.43	0.0918	0.0937
47	2.0	75.76	17.66	6.58	0.0836	0.0153
48	2.0	71.37	15.28	13.35	0.0645	0.0217
49	2.0	68.49	20.27	11.76	0.0563	0.1232
50	2.0	61.48	22.06	16.56	0.1482	0.0205
51	2.0	56.14	28.85	15.01	0.2213	0.0922
52	2.0	67.19	13.74	19.07	0.1622	0.0829
53	2.0	64.87	24.04	11.09	0.0637	0.0616

Experiment No. 18 to 21 are the data in equilibrium with the SiO_2-CaO binary slags

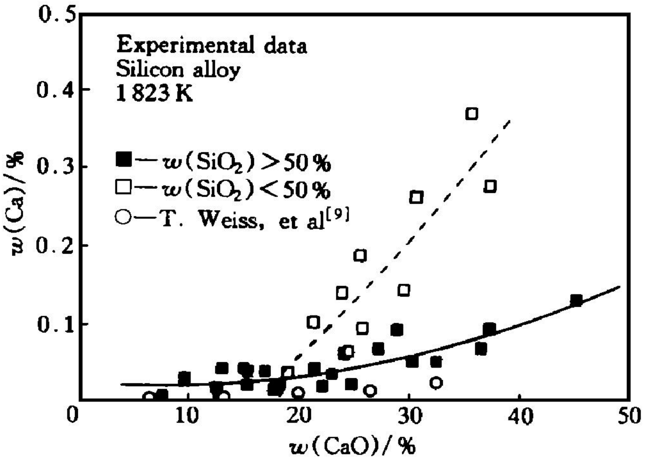

Fig. 5 Relations of Ca content in silicon and CaO content in slag at 1 550 ℃

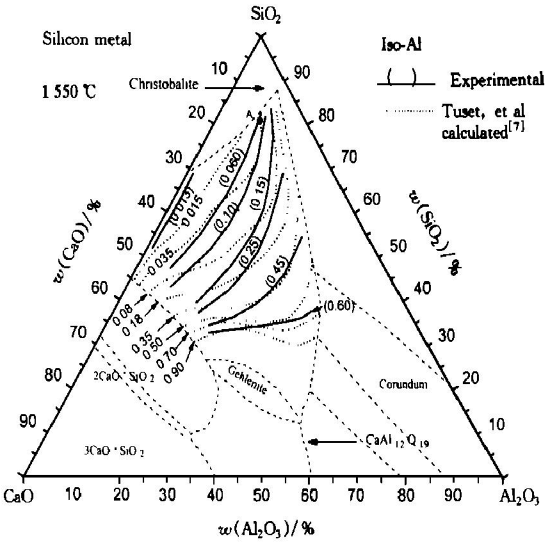

Fig. 6 Comparison of iso-Al concentration curves between experiment and calculation[7]

aluminium and calcium in equilibrium with the slag system of SiO_2-Al_2O_3-CaO at 1 550 ℃.

The distributions are given in terms of iso-concentration curves for Al and Ca in silicon. The isoconcentration curves calculated by Schei et al[7] are also listed in Fig. 6 and Fig. 7. It is clearly that the change direction of the curves agrees very well between the present work and the calculated. Since we can not measure all of the compositions in silicon and slag, the present work may provide valuable data to

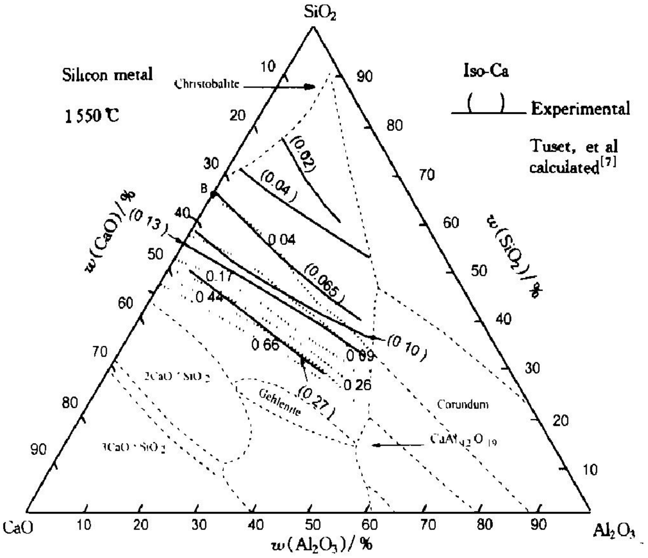

Fig. 7 Comparison of iso-Ca concentration curves between experiment and calculation[7]

analyze the action of aluminium and calcium during the oxidation refining process.

5 CONCLUSIONS

The equilibria of Al and Ca between silicon alloys and SiO_2-CaO-Al_2O_3 ternary slags were investigated using graphite crucible at 1 550 ℃. The distributions of aluminium and calcium between silicon alloy and ternary slags were obtained. With increasing Al_2O_3 and CaO content in the slag, the Al and Ca content increase respectively. The variation of the impurities is also affected by the silica content in slag which provides the oxidant during the oxidation refining process.

The distributions are given in terms of isoconcentration curves for Al and Ca in silicon. The present experimental work provides available data to analyze the action of Al and Ca during oxidation refining process for silicon alloy.

ACKNOWLEDGMENTS

The authors express their thanks to SUN Ming-shan, YE Bin, ZHOU Can-dong and YOU Jing-lin for the help during the experiments. Financial support provided by Shanghai Science and Technology Committee is also acknowledged.

[REFERENCES]

[1] Schei A, Tuset J Kr, Tveit H. Production of High Silicon Alloys [M]. Tapair Forlag, Trondheim, Norway, 1998. 13- 20.

[2] Juneja J M, Mukherjee T K. A study of the purification metallurgical grade silicon [J]. Hydrometallurgy, 1986, 16: 69- 75.

[3] Voos W. Method of Purifying Silicon [P]. US Patent 2972521. 1961.

[4] Hunt L P, Dosaj V D, McCormick J R, et al. Production of solargrade silicon from purified metallurgical silicon [A]. Record of the 12th IEEE Photovoltaic Specialists Conference [C]. New York, 1976. 125.

[5] Hunt L P, Dosaj V D, McCormick J R, et al. Purification of metallurgical grade silicon to solar grade quality [A]. Solar Energy, Proc Intern Symp [C]. Electrochemical Society, New York, 1976. 200.

[6] Chu T L, Chu S S. Partial purification of metallurgical silicon by acid extraction [J]. J Electrochem Soc, 1983, 30: 455- 461.

[7] Schei A, Tuset J Kr, Tveit H. Production of High Silicon Alloys [M]. Tapair Forlag, Trondheim, Norway, 1998. 265- 268.

[8] Holta H. Tinject Refining During 15 Years [A]. INFACON 7 [C]. Trondheim, Norway, 1995. 463- 472.

[9] Weiss T, Schwerdfeger K. Chemical equilibria between silicon and slag melts [J]. Metallurgical and Materials Transactions B, 1994, 25(8): 497- 504.

[10] WU Xian-xi. Activity calculations of each component in Al-Si-Fe ternary system [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 1999, 9(3): 627- 630.

[11] Rein R H, Chipman J. Activities in the liquid solution SiO_2-CaO-MaO-Al_2O_3 at 1 600 ℃ [J]. Transactions of The Metallurgical Society of AIME, 1965, 233(2): 415- 425.

[12] Ottem L. Equilibria between Molten Silicon and SiO_2-CaO-Al_2O_3 Slags at 1550 ℃ [R]. SINTEF Report STF34 F93112, 1993, Norway.

[13] Margaria T. Silicon refining: Experimental studies and industrial means to control silicon quality in silicon for the chemical industry III [R]. Øye H A, Rong H A, Ceccaroli B, et al. Norw University of Sci and Techn. Norway, 1996, 21- 32.

[14] Kay D, Taylor J. Trans Faraday Soc, 1960, 56: 1372.

[15] Ohta H, Suito H. Activities in CaO-SiO_2-Al_2O_3 slags and deoxidation equilibria of Si and Al [J]. Metall and Mater Trans B, 1996, 27B(12): 943- 949.

(Edited by YUAN Sai-qian)