Manganese and Silicon Distribution between Slag and Metal in Silicomanganese Production

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(Received on February 21, 2000; accepted in final form on May 23, 2000)

Laboratory measurements have been carried out to investigate the equilibrium distribution of manganese and silicon between slag and metal in silicomanganese production. Graphite crucibles have been used to study equilibrium between Mn–Si–C_{sat} alloys and MnO–SiO₂–CaO–Al₂O₃–MgO slags in CO gas at 1 600°C, 1 650°C and 1 700°C.

The equilibrium content of Si in the metal is mainly controlled by the temperature, the silica content of the slag and the mass ratio $R = (\text{CaO} + \text{MgO})/\text{Al}_2\text{O}_3$. The silicon content increases with the temperature and the silica content, and decreases with increasing R -ratio. The silicon content remains approximately the same when some MgO replaces CaO in the slag.

The equilibrium content of MnO in silicomanganese slags is primarily controlled by the temperature and the silica content of the slag. Addition of Al₂O₃ to acid slags will result in somewhat lower MnO contents, and addition to more basic slags has the opposite effect. The equilibrium content of MnO in the slag is slightly increased when some CaO is replaced by MgO.

KEY WORDS: silicon distribution; manganese distribution; silicomanganese; equilibrium relations; equilibrium diagrams.

1. Introduction

The distribution of silicon and manganese between carbon-saturated Mn–(Fe)–Si–C alloys and MnO–SiO₂–CaO–Al₂O₃–MgO slags in equilibrium with CO gas is a result of simultaneous reactions taking place on production of manganese ferroalloys, especially silicomanganese. In this process the temperature may reach 1 600°C or higher, and the composition of metal and slag is assumed to approach equilibrium. Due to its importance, and for a better understanding of the processes, equilibrium measurements have been carried out by a number of investigators.^{1–12)}

The basic reactions between slag, metal and the gas phase are described by the following equations:

where parentheses denote the slag phase and underscored the alloy phase.

The present authors have previously defined the simultaneous establishment of the two equilibria as complete slag/metal/gas equilibrium. In recent years laboratory measurements have been conducted to determine complete equilibrium in the following systems^{1–3)}:

(1) Mn–Si–C_{sat} alloys and slags in the systems MnO–SiO₂–CaO and MnO–SiO₂–CaO–Al₂O₃ in the temperature range 1 450°C to 1 600°C.¹⁾ However, the results at 1 600°C

were not sufficient for a complete description of equilibrium relations at elevated temperatures.

(2) Mn–Fe–Si–C_{sat} alloys and synthetic and industrial multicomponent slags in the temperature range 1 350°C to 1 500°C.^{2,3)}

Figure 1 illustrates complete equilibrium relations between Mn–Fe(10%)–Si–C_{sat} alloys and five component MnO–SiO₂–CaO–Al₂O₃–MgO slags, with mass ratios

Fig. 1. Slag/metal/gas equilibrium diagram²⁾ for carbon saturated Mn–Fe–Si–C alloys and MnO–SiO₂–CaO–Al₂O₃–MgO slags at $P_{\text{CO}} = 1$ atm, the shaded area being of interest in the present study.

$\text{CaO}/\text{Al}_2\text{O}_3=1.5$ and $\text{MgO}/\text{Al}_2\text{O}_3=0.8$, at various temperatures and $P_{\text{CO}}=1$ atm.²⁾ It was found that the state of complete equilibrium is very dependent on the temperature and on the pressure of the system. In contact with identical alloys, higher temperatures and higher slag basicities will give lower MnO contents in the slag.

A combination of the two equilibrium reactions above will give the slag/metal equilibrium reaction, expressed by

When only the slag/metal equilibrium is established, the system is said¹⁾ to be at partial slag/metal equilibrium. This reaction is little dependent on the temperature and independent of the pressure and composition of the gas phase. Experimental results of partial slag/metal equilibria have been reported in the literature.¹⁻⁹⁾ It is strongly emphasized that partial slag/metal equilibrium alone will not describe completely the final composition of the melts in a carbothermic process.

High process temperatures are required for production of silicomanganese alloys by carbothermic reduction of the oxide ores. According to industrial specifications, the contents of Mn and Si in the alloy vary from 60 to 70% and from 15 to 33%, respectively. Based on previous estimation,²⁾ the maximum Si content of the Mn-Si-C_{sat} alloys will be about 24% Si at 1600°C and 32% Si at 1700°C, assumed unit activity of SiO₂ and a total pressure of one atmosphere, *i.e.* $P_{\text{CO}} + P_{\text{SiO}} + P_{\text{Mn}} = 1$ atm.

The present study focuses on complete slag/metal/gas equilibrium relations between Mn-Si-C_{sat} alloys and MnO-SiO₂-CaO-Al₂O₃-MgO slags in CO gas (1 atm) at 1600°C and higher. The investigated slag compositions are limited to the low MnO side, as illustrated by the shaded area in Fig. 1. The equilibrium compositions are measured experimentally by using a slag-metal-gas equilibrium technique with a large metal/slag ratio.

2. Experimental

2.1. Furnace Design

A vertical furnace with a graphite heating element was used for the equilibrium measurements. The furnace assembly is shown in Fig. 2. The furnace consists of two parts, one for keeping the graphite crucible at the reaction temperature, and the other for quenching in a water-cooled jacket which allows the sample to retain its equilibrium composition.

The connection between the two parts consists of a stainless tube carrying a graphite supporter. A gas-tight motion structure is designed at the bottom of the quenching zone, so the steel tube can slide easily up and down.

The temperature profile was measured in advance. It was found that the lower position of the constant hot zone was near the bottom of the crucible. According to experience from previous measurements,¹²⁾ the temperature readings on a thermocouple in close contact with the bottom of the crucible will be 8–12°C lower than the real temperatures in melts. A correction had therefore to be made for this temperature difference.

Cylindrical graphite blocks were used as crucibles in all experiments. Each block had four holes acting as separate

Fig. 2. Furnace arrangement.

containers. For the highest temperatures and slags with high silica contents, a deeper crucible was required. It is because the acid slags have a tendency to climb high up along the crucible wall. A graphite lid was also needed, especially at higher temperatures, to prevent soot from the top of the furnace to fall into crucibles. When the silicon content of the alloy exceeds the graphite/SiC coexistence point, *e.g.* about 19.1% at 1600°C, the stable carbon-containing phase is silicon carbide rather than graphite. Also in this case the graphite crucibles can be employed with safety because the inside of the graphite crucible wall will be covered with a dense layer of SiC.¹²⁾

2.2. Experimental Procedure

Master alloys and slags were made by mixing and pre-melting reagent grade chemicals at desired ratios in an induction furnace. Graphite crucibles were used. Prepared alloys and slags were charged in each crucible hole, 8.5 g of metal and 1 g of slag, and the graphite crucible was placed in the hot zone of the furnace. The system was sealed and evacuated by a rotary pump. Afterwards CO gas was gradually filled into the furnace. The electric power should be supplied at a medium rate to avoid thermal shock on the hot parts of the furnace and massive evolution of CO gas from the reaction area. The temperature was controlled and monitored by a thermocouple on the outside wall of the heating element. Regular temperature calibrations were carried out by using a thermocouple underneath the crucible.

The necessary time to reach equilibrium had been determined earlier.¹²⁾ Less time was required if a large metal/slag ratio was used in the experiment. The samples were held at the reaction temperature for about 3 hr at 1700°C and 5 hr at 1600°C. During heating, the flow rate of CO gas was about 15 l/hr.

At the end of the run, the crucible was withdrawn immediately to the quenching zone. Metal and slag were carefully separated from the crucible, and adherent graphite was removed by grinding with sandpaper. The Si content of the metal sample was analysed by the ICP method that was checked against the conventional gravimetric method. The slag samples were analysed by electron microprobe analysis.

The equilibrium gas composition for the system Mn–Si–C–O was calculated,¹²⁾ assuming unit activity of SiO_2 , carbon saturation, and a total pressure of one atm:

Temperature	P_{CO}	P_{SiO}	P_{Mn}
1600 °C	0.969	0.022	0.004
1650 °C	0.942	0.050	0.003
1700 °C	0.887	0.106	0.003

In case of SiO -saturation, an extensive loss of silicon to the escaping gas would be experienced due to the employed CO flow rate. However, a silicon balance indicated that the real Si loss was less than 0.3 g. Then the real partial pressures were estimated to be $P_{\text{SiO}}=0.0032$ atm and $P_{\text{CO}}\cong 1$ atm.

2.3. Observations

Some significant observations were made at the high temperature measurements. When experiments were carried out below 1600°C, the cross sections of the crucibles were as shown in Figs. 3(a) and 3(b). For Si contents of the metal less than about 20%, the slag covered and wetted the metal slightly better than it wetted the graphite as described by Fig. 3(a). For higher Si contents, which also means increased silica contents of the slag, the slag showed higher affinity to the crucible wall, represented by Fig. 3(b). In such cases, removal of adherent graphite from the slag was a difficult task. However, the wetting of the graphite did not violate the accomplishment of the experiments.

More trouble arose with further increase in temperature, especially for experiments with higher Si contents of the metal, say above 20%. The higher the Si content, the higher the slag climbed on the crucible wall, see Figs. 3(c) and 3(d). In the extreme case, the inside wall of the crucible was completely covered by a thin layer of slag, and it was impossible to sample the slag for analysis. This is illustrated in Fig. 3(d). Sometimes green materials, probably SiC and mixtures of SiC and slag, were found in the upper part of the crucible, see Figs. 3(e) and 3(f). This material was not in contact with the metal and was not considered to be at equilibrium. Up to now there is no good explanation of

this phenomenon.

For experiments with high Si contents of the metal, a rugged hole was created on the top of the solidified metal. Sometimes, after running experiments with high Si metal at high temperatures, most of the metal had escaped from the crucible.

3. Results and Discussion

The results of all equilibrium measurements at 1600°C, 1650°C and 1700°C are given in Table 1. 12 experiments were carried out at 1600°C, mostly with 4 samples in each graphite block, in total 45 samples. 24 samples from previous measurements¹⁾ at 1600°C are also included at the end of the table. 9 experiments with 33 samples were run at 1650°C, and 4 experiments with 14 samples at 1700°C. The final Si and Mn distribution between slag and metal were determined for different mass ratios of $(\text{CaO}+\text{MgO})/\text{Al}_2\text{O}_3$ and of CaO/MgO . These oxides are not reduced to any measurable extent so the ratios remain unchanged during the experiment.

3.1. The Equilibrium Content of MnO in Slag

A typical result of complete slag/metal/gas equilibrium at 1600°C is shown in Fig. 4. In these experiments MnO– SiO_2 –CaO– Al_2O_3 slags with mass ratio $\text{CaO}/\text{Al}_2\text{O}_3=4$ were used. A minimum equilibrium content of MnO in the slag is observed near 44% SiO_2 . Results obtained with ternary MnO– SiO_2 –CaO slags are also shown for comparison (rhombs). Such minimum contents of MnO were not emphasized in previous equilibrium measurements^{1–3)} mostly carried out at lower temperatures, see Fig. 1.

The relation between activity and concentration of MnO may cause this abnormal behaviour. Figure 5 shows the activity of MnO in MnO– SiO_2 –CaO slags at 1500°C. The solid activity lines refer to pure solid MnO and were measured by Abraham *et al.*¹³⁾ The long-dash lines give a hypothetical image of the MnO activity in the whole region, now with pure liquid MnO as standard. These latter activities were calculated using the random network model by

Fig. 3. Schematic cross sections of crucibles after experiments.

Fig. 4. Equilibrium compositions of MnO– SiO_2 –CaO– Al_2O_3 slags with mass ratio $\text{CaO}/\text{Al}_2\text{O}_3=4$ at 1600°C.

Table 1. Experimental conditions and equilibrium compositions of Mn-Si-C_{sat} alloys and MnO-SiO₂-CaO-Al₂O₃-MgO slags at various temperatures and $P_{CO}=1$ atm.

Samp. No.	Temp. °C	Time h	M/S ratio	Initial composition (mass%)			Final composition (mass%)					
				Metal			Slag					
				Si	SiO ₂	MnO	Si	SiO ₂	MnO	CaO	Al ₂ O ₃	MgO
D11	1600	4.5	5.82	22.32	62.11	5.17	21.5	37.98	2.20	27.82	32.01	
D12			5.03	16.73	43.16	2.53	17.2	27.51	0.75	36.99	34.75	
D13			6.41	7.00	35.0	0	6.2	28.62	3.28	34.50	33.60	
D14			5.28	3.53	35.0	0	4.9	30.56	4.95	32.53	31.96	
D21	1600	4.5	6.81	22.28	61.91	5.59	22.4	52.00	6.46	14.97	14.69	11.87
D22			6.24	16.74	42.46	3.55	17.2	43.21	4.17	19.00	18.33	15.29
D23			8.14	6.91	35.0	0	6.8	34.05	5.22	22.69	21.26	16.77
D24			6.37	3.66	35.0	0	3.6	31.57	6.01	22.80	21.89	17.64
D31	1600	4.5	6.65	22.56	61.78	5.97	21.5	55.49	6.12	30.47	7.90	
D32			6.07	16.51	42.5	5.5	17.3	44.30	2.07	42.60	11.04	
D33			7.29	7.06	35.0	0	5.9	40.62	4.53	43.94	10.91	
D34			6.37	3.55	35.0	0	2.8	37.91	6.59	44.24	11.26	
D41	1600	5.0	6.78	22.29	62.27	5.97	22.0	53.13	6.12	19.89	5.20	15.46
D42			6.06	16.49	43.21	4.20	17.3	46.81	3.44	24.58	6.14	19.03
D43			7.18	7.0	35.0	0	6.0	39.59	6.71	26.49	6.78	20.44
D44			7.08	3.68	35.0	0	2.8	36.21	7.39	27.84	7.08	21.48
D51	1600	5.0	7.57	24.78	55	0	23.6	59.20	8.71	17.50		14.59
D52			9.54	25.21	55	0	23.9	61.82	7.44	15.45	15.29	
D53			7.80	12.17	40.96	0	14.9	36.87	3.30	30.45	29.39	
D54			8.25	5.77	35.0	0	6.6	31.05	5.23	32.58	31.14	
D61	1600	4.5	8.42	19.05	39.46	3.27	19.7	39.19	2.43	29.92	28.46	
D62			8.40	15.49	38.14	3.24	17.1	39.13	3.56	29.24	28.06	
D63			8.38	19.09	47.70	3.20	20.2	46.31	2.93	40.55	10.20	
D64			8.29	15.65	41.49	4.76	17.1	44.06	2.55	42.71	10.67	

Samp. No.	Temp. °C	Time h	M/S ratio	Initial composition (mass%)			Final composition (mass%)					
				Metal			Slag					
				Si	SiO ₂	MnO	Si	SiO ₂	MnO	CaO	Al ₂ O ₃	MgO
D211	1700	3.0	8.51	6.25	41.35	4.40	6.45	36.22	3.48	46.46	13.84	
D212			8.28	6.36	42.25	5.34	6.78	23.57	2.45	38.87	35.11	
D213			8.21	14.09	47.50	3.70	14.06	37.80	1.39	48.89	11.92	
D214			8.50	13.86	45.79	2.72	14.15	29.27	1.97	35.75	33.01	
D221	1700	3.0	8.42	14.00	45.64	5.46	14.33	40.47	1.86	31.28	8.32	18.07
D223			8.32	14.00	46.07	5.34	14.98	31.79	2.03	27.95	26.08	12.15
D241	1700	3.0	8.22	7.04	35.48	2.64	6.92	38.04	3.71	29.25	7.86	21.14
D242			7.85	20.09	46.19	2.52	19.18	41.20	1.25	36.21	10.05	11.29
D243			7.29	7.01	35.0	0	7.37	31.13	3.13	24.82	22.80	18.12
D244			7.96	20.0	41.48	2.55	17.60	32.91	1.52	27.20	26.66	11.72
D251	1650	4.0	8.55	25.3	54.46	5.46	23.05	49.85	2.17	30.90	2.84	14.25
D252			8.58	25.28	52.25	5.5	23.77	48.35	2.40	33.27	9.15	6.83
D254			8.53	25.55	49.0	5.5	23.88	41.75	2.39	26.87	27.57	1.42
D261	1700	3.0	8.62	19.84	45.25	2.75	17.35	42.38	0.14	45.26	11.22	1.00
D262			8.21	19.84	46.10	3.41	19.40	28.56	0.92	36.15	34.37	
D263			8.41	19.63	50.0	0	18.73	44.52	1.24	41.54		12.70
D264			8.27	10.76	50.0	0	11.12	43.16	2.74	32.75		21.35
D272	1650	4.0	8.55	20.82	52.25	2.75	19.85	45.29	1.75	27.63	8.75	16.58
D273			8.47	16.04	45.64	5.45	15.52	43.79	3.14	27.27	6.63	19.18
D274			8.37	8.03	42.99	5.39	8.22	39.89	3.71	28.16	7.42	20.81

(previously published results)

Samp. No.	Temp. °C	Time h	M/S ratio	Initial composition (mass%)			Final composition (mass%)					
				Metal			Slag					
				Si	SiO ₂	MnO	Si	SiO ₂	MnO	CaO	Al ₂ O ₃	MgO
D71	1600	5.0	8.97	15.19	39.95	4.63	16.8	42.23	4.32	20.02	18.83	14.60
D72			8.44	12.22	39.55	3.81	13.9	40.79	5.18	20.34	18.83	14.86
D73			8.55	9.63	38.7	6.05	12.0	39.29	5.95	20.81	19.07	14.88
D81	1600	4.5	8.52	26.42	75	0	24.0	72.81	6.32	10.35	10.53	
D82			8.26	27.12	70	0	24.1	69.99	7.82	8.25	7.96	5.98
D83			8.51	27.12	60	0	23.4	58.71	11.56	24.21	5.53	
D84			8.35	27.63	75	0	24.0	77.00	6.08	8.05	8.87	
D91	1650	4.2	8.31	26.13	64.76	7.48	24.4	46.35	3.42	19.58	18.44	12.21
D92			8.28	20.00	60.78	6.41	21.0	39.17	2.18	24.90	23.01	10.74
D93			8.23	17.36	55.53	6.35	19.3	40.46	2.43	22.52	20.98	13.61
D94			8.34	15.20	53.28	5.93	17.6	39.37	3.39	22.83	21.00	13.41
D101	1650	4.0	8.28	29.16	67?	5?	26.5	66.48	8.81	9.24	8.84	6.64
D102			8.48	19.95	55.74	5.39	20.4	36.82	1.54	31.63	30.02	
D103			8.30	17.28	49.85	5.34	19.0	38.06	2.57	30.47	28.90	
D104			8.66	15.22	45.86	5.56	16.5	37.74	2.83	30.33	29.09	
D111	1600	5.0	8.59	14.19	43.23	5.56	15.7	46.53	4.62	24.55	6.17	18.12
D112			8.51	20.03	50.3	5.5	20.1	49.21	2.91	25.02	6.47	16.39
D113			8.44	20.04	52.72	5.45	19.4	45.22	4.42	25.42	24.94	
D114			9.5	19.03	35.0	0	10.5	49.56	3.25	27.33		19.87
D121	1650	4.0	8.44	14.04	38.71	2.72	13.42	41.09	2.35	45.14	11.42	
D122			8.46	17.59	41.96	3.24	16.03	42.93	1.99	43.89	11.19	
D123			8.61	21.04	45.9	2.75	20.13	43.08	1.02	44.56	11.35	
D124			8.18	24.46	51.83	3.17	21.97	44.44	1.62	42.91	11.03	
D131	1600	5.0	8.61	21.06	52.88	4.44	19.36	48.75	3.88	37.59	9.78	
D134			8.64	20.33	47.63	4.44	19.59	46.89	4.97	17.74	16.94	13.46

Samp. No.	Temperature (°C)	Initial composition (mass%)			Final composition (mass%)					
		Metal			Slag					
		Si	SiO ₂	MnO	Si	SiO ₂	MnO	CaO	Al ₂ O ₃	MgO
TC-1 <i>Ref. 1</i>	1600				21.51	60.04	12.62	27.33		
TC-2 "					19.63	54.41	7.87	37.71		
TC-3 "					17.37	51.36	7.21	41.42		
TC-4 "					13.34	49.18	7.0	43.82		
TC-5 "					23.90	60.35	9.07	30.58		
TC-6 "					20.64	52.83	6.17	40.99		
TC-7 "					13.25	47.15	3.96	48.88		
TC-8 "					7.34	41.49	4.74	53.77		
QA-1 <i>Ref. 1</i>	1600				22.1	57.32	7.35	21.58	13.57	
QA-2 "					20.0	48.11	4.87	28.21	18.81	
QA-3 "					16.1	45.85	2.79	31.84	19.52	
QA-4 "					14.7	41.59	2.17	34.48	21.73	
QA-5 "					8.0	33.7	9.7	39.9	16.7	
QA-6 "					1.4	29.5	5.7	40.9	23.9	
QA-7 "					22.0	61.05	9.04	18.4	11.51	
QA-8 "					10.75	36.95	4.79	36.13	22.13	
QB-1 <i>Ref. 1</i>	1600				17.38	45.75	3.06	38.4	12.75	
QB-2 "					9.03	38.03	2.82	44.67	14.49	
QB-3 "					2.52	32.4	5.0	45.7	16.9	
QB-4 "					20.52	50.3	5.37	33.4	10.9	
QB-5 "					1.5	32.3	4.5	47.1	16.1	
QB-6 "					21.26	54.25	7.97	26.12	11.65	
QB-7 "					5.77	35.9	5.58	43.31	15.21	
QB-8 "					24.12	61.72	8.77	22.19	7.31	

Samp. No.	Temp. °C	Time h	M/S ratio	Initial composition (mass%)			Final composition (mass%)					
				Metal			Slag					
				Si	SiO ₂	MnO	Metal	Si	SiO ₂	MnO	CaO	Al ₂ O ₃
D141	1650	4.0	8.32	27.63	58.79	5.87		42.64	1.57	25.72	25.80	4.27
D142			8.29	27.73	55.53	5.34		44.64	2.02	24.65	23.29	5.40
D143			8.49	10.51	36.0	5.5	10.65	35.73	4.38	23.31	21.82	14.76
D144			8.55	24.63	55.20	5.93		40.95	2.33	27.59	26.47	2.66
D151	1600	5.0	8.48	20.30	50.95	5.5	18.62	50.36	4.85	22.68	5.82	16.27
D152			8.53	12.30	42.5	5.5	11.68	44.89	5.19	25.62	6.42	18.07
D153			8.25	24.49	56.89	5.87	20.53	52.46	5.12	33.66	8.76	
D154			8.52	25.17	55.5	5.5	20.51	51.60	6.85	15.40	14.99	11.17
D161	1650	4.0	8.50	24.49	52.9	5.5		43.41	1.85	28.95	17.35	8.45
D162			8.49	24.47	49.65	5.5		43.37	1.93	28.66	17.44	8.60
D163			8.51	15.04	39.25	5.5		41.69	2.51	29.57	17.52	8.71
D164			8.50	24.49	42.5	5.5		43.05	1.66	29.17	17.68	8.44
D171	1600	5.0	8.36	24.36	55.74	5.39	22.60	53.50	6.22	21.90		18.38
D172			8.26	20.96	54.81	5.87	19.67	51.44	4.93	23.95		19.68
D173			8.89	15.75	49.74	2.86	15.64	48.20	4.91	25.53		21.36
D174			8.46	6.97	49.75	2.72	6.93	41.90	4.89	32.01		21.19
D181	1650	4.0	8.33	29.01	65.39	5.93	24.33	49.74	2.65	35.10	12.52	
D182			8.54	27.24	60.7	5.50	24.09	47.74	2.58	36.79	12.89	
D183			7.94	6.47	42.37	5.40	9.94	38.98	3.98	41.61	15.23	
D184			8.43	27.29	60.54	5.99	24.32	47.48	2.49	36.80	13.43	
D201	1650	4.0	8.96	21.11	49.74	2.86	20.26	47.94	2.31	29.72		20.03
D202			8.74	7.91	49.55	4.95	9.65	43.02	4.87	31.08		21.04
D204			8.55	8.14	36.00	5.50	8.60	28.15	2.73	35.18	33.94

Fig. 5. Iso-activity curves of MnO in MnO-SiO₂-CaO melts at 1500°C. The solid lines given by Abraham *et al.*¹³⁾ refer to pure solid MnO. The model calculated long-dashed lines refer to pure liquid MnO.

	CaO Al ₂ O ₃	CaO MgO	R= CaO+MgO Al ₂ O ₃
△	1	∞	1
◇	1	1.5	1.7
□	4	∞	4
○	4	1.5	6.7

Fig. 6. Equilibrium relations for MnO-SiO₂-CaO-Al₂O₃-MgO slags with different *R*-ratios at 1650°C and 1700°C. *R*=mass ratio (CaO+MgO)/Al₂O₃.

Yokokawa and Niwa.¹⁴⁾ The activity lines indicate that the activity coefficient of MnO approaches a maximum near the mole ratio of CaO/SiO₂ equal to 2. On the pseudobinary line MnO-Ca₂SiO₄, more free oxygen ions, O²⁻ are released due to the strong affinity between (SiO₄)⁴⁻ anions and Ca²⁺ cations. This is quite similar to what is observed in the better known system FeO-SiO₂-CaO.

Figure 6 shows how the complete equilibrium curves at 1650°C and 1700°C change with the value of *R**, which is defined as the ratio of the sum of basic oxides (CaO+MgO)

	CaO Al ₂ O ₃	CaO MgO	R= CaO+MgO Al ₂ O ₃		CaO Al ₂ O ₃	CaO MgO	R= CaO+MgO Al ₂ O ₃
△	1	∞	1	□	4	∞	4
◇	1.5	∞	1.5	△	4	1.5	6.7
☆	1	1.5	1.7	⊗	∞	1.5	∞
◇	2.8	∞	2.8	○	∞	∞	∞

Fig. 7. MnO versus SiO₂ in multicomponent slags at 1600°C shown for various component mass ratios.

to Al₂O₃. This parameter has previously⁹⁾ been shown to be of considerable importance for the distribution of silicon and manganese between slag and metal. With a decrease in the *R* value from 4 to 1, the silica content at the minimum point drops from 43 % to 31 % at 1650°C, and from 42.5 % to 27 % at 1700°C.

A considerable influence of the temperature on the distribution equilibria has been verified experimentally. The equilibrium content of MnO in the slag decreases with increasing temperature as shown in the Figs. 1, 6 and 8. Figures 6 and 8 also indicate that the MnO minimum point shifts to lower silica contents with increasing temperature.

The relationship between MnO and SiO₂ at 1600°C is shown in **Fig. 7**. Curves are drawn for *R*-values between 1 and 6.7. CaO/MgO ratios are also given. The V-type curves get more open with a decrease in the *R*-values. Replacement of CaO with MgO shifts the curve upwards a little, and addition of more alumina shifts the curve to the left. Alumina is characterised as an amphoteric oxide. When added to acid slags, Al₂O₃ will act as a basic component and give lower MnO contents, and addition to more basic slags will have the opposite effect. The change between 'acid' and 'basic' slags takes place at about 45 % SiO₂. For a typical silicomanganese slag with about 40 % SiO₂ the effect of Al₂O₃ addition will be to decrease the MnO content somewhat in the slag.

3.2. Distribution of Silicon between Slag and Metal

The equilibrium distribution of silicon between Mn-Si-C_{sat} alloys and MnO-SiO₂-CaO-Al₂O₃ slags with mass ratio CaO/Al₂O₃=4 at 1600°C, 1650°C and 1700°C is shown in **Fig. 8**. The measurements with high silica slags at 1700°C were not successful. The reason is that insufficient amounts of slag for chemical analysis were left in the cru-

* *R*=mass ratio (CaO+MgO)/Al₂O₃

Fig. 8. Equilibrium relations for MnO-SiO₂-CaO-Al₂O₃ slags with mass ratio CaO/Al₂O₃=4 at 1600°C, 1650°C and 1700°C.

cible. A thin layer of slag, covering the inside and outside wall of the graphite crucible, was usually observed after experiments at high temperatures and with high silica contents. The explanation is that very strong wetting between high silica slag and graphite forced the slag to climb out of the crucible.

Solid lines and marks, refer to the right y-axis, giving the silicon content of the alloy *versus* the silica content of the slag. The long-dashed elongation of the 1700°C curve indicates an expected relation. The silicon content of the alloys increases fast with increasing silica in the slag up to about 18–20% Si. Then follows a slow increase until silica saturation is reached. The change in slope is a result of carbon being replaced by silicon carbide as the stable carbon-containing phase.⁹⁾

The effect of temperature on the silicon distribution is considerable. As shown in Fig. 8, the equilibrium content of silicon in the alloy increases with about 6% per 50°C in the temperature range 1600°C to 1700°C. It also appears from the figure that the equilibrium content of SiO₂ in the slag, for a certain Si-content of the metal, decreases with about 2% for an increase in the temperature of about 50°C.

The equilibrium content of MnO is also shown in Fig. 8, here as chain-dashed lines and open marks. As mentioned before, the position of the MnO-minimum shows to be a function of the temperature. A comprehensive information about the complete equilibrium relations is obtained by, at the same time, reading the curves showing Si vs. SiO₂ and MnO vs. SiO₂.

The Si distribution is also dependent on other slag components and their ratios. The equilibrium distribution of silicon between metal and slag at 1600°C is shown for various slags at 1600°C in Fig. 9. The same relation is shown in Fig. 10 for the equilibrium distribution of Si at 1650°C. The *R*-value is the major parameter determining the position of the equilibrium curves. The CaO/MgO ratio is of minor importance.

Fig. 9. Distribution of silicon as a function of the mass ratio $R=(\text{CaO}+\text{MgO})/\text{Al}_2\text{O}_3$ at 1600°C.

Fig. 10. Distribution of silicon as a function of the mass ratio $R=(\text{CaO}+\text{MgO})/\text{Al}_2\text{O}_3$ at 1650°C.

Fig. 11. Comparison of the Si distribution between metal and slag for Mn-Si-C_{sat} and Fe-Si-C_{sat} alloys¹⁵⁾ at 1600°C.

Fig. 12. Maximum Si content of Mn-Si-Csat alloys in equilibrium with silica-saturated slags at 1600°C and 1650°C.

A comparison of the silicon distribution between slag and metal for Mn-Si-C_{sat} and Fe-Si-C_{sat}¹⁵⁾ alloys at 1600°C is made in Fig. 11. In principle, the difference between the two systems is that only silicon is distributed between the condensed phases in the iron system, whereas both Si and Mn are distributed in the manganese system. Otherwise the two systems are quite similar.

3.3. The Silicon Content of Alloys Equilibrated with Silica-saturated Slags

Figure 12 shows the the silicon content of Mn-Si-C_{sat} alloys versus the silica content of MnO-SiO₂-CaO-Al₂O₃-MgO slags in CO gas atmosphere. Solid marks indicate the starting composition of the metal melts and the arrows show the direction of approach to equilibrium. In contact with silica-saturated slags, the maximum silicon content appears to be 24.0% Si at 1600°C and 26.5% Si at 1650°C. For comparison, the equilibrium content of silicon in Fe-Si-C_{sat} alloys, also in contact with silica-saturated slag, have been reported¹⁵⁾ to be 26.1% Si at 1600°C.

4. Conclusions

The equilibrium content of MnO in silicomanganese slags depends first of all on the temperature and secondly on the silica content of the slag. At 1600°C the MnO content decreases from about 9% at silica saturation to a minimum of about 2–4% when the silica content is reduced to about 40–45%. The equilibrium content of MnO in the slag is slightly increased when some CaO is replaced by MgO.

Addition of Al₂O₃ to acid slags will result in lower MnO contents, and addition to more basic slags has the opposite effect, that is to increase MnO in the slag. The change between 'acid' and 'basic' slag takes place at about 45% SiO₂, so for typical silicomanganese slags with about 40%

SiO₂, the effect of Al₂O₃ will be to decrease the equilibrium content of MnO somewhat in the slag.

The distribution of Si between Mn-Si-C_{sat} alloys and multicomponent MnO-SiO₂-CaO-Al₂O₃-MgO slags is mainly determined by the temperature, the silica content of the slag and the *R*-ratio=(CaO+MgO)/Al₂O₃.

The effect of temperature on the silicon distribution is considerable. The equilibrium silicon content of the alloy increases with about 6% per 50°C in the temperature range 1600°C to 1700°C.

The silicon content of the alloy increases fast with increasing silica in the slag up to about 18–20% Si. Then follows a slow increase until silica saturation is reached. The change in slope is a result of carbon being replaced by silicon carbide as the stable carbon containing phase. The maximum Si-content is about 24% at 1600°C and 26.5% at 1650°C.

The *R*-ratio=(CaO+MgO)/Al₂O₃ influences strongly the SiO₂-activity of the slag and thereby the Si-content of the equilibrated alloy. As an example, an alloy in equilibrium with a slag of fixed silica content at 1600°C will increase its Si-content with about 8%, say from 12 to 20%, when the *R*-ratio is increased from 1 to 2. The silicon content of the metal remains approximately the same when MgO replaces some CaO in the slag.

Acknowledgments

The research work has been financially supported by the Research Association of The Norwegian Ferroalloy Producers (FFF) and the Research Council of Norway (NFR). They are gratefully acknowledged.

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