

Determination of component activities in the Cr-Si-C and Cr-Fe-Si-C melts

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ABSTRACT

The purpose of the present investigation is an experimental determination of the component activities in the carbon saturated Cr-Si-C and Cr-Fe-Si-C systems. The measurements were carried out by use of the mass spectrometric technique.

Activities of chromium and iron were determined for the following systems: Cr-Si-C_{sat} at 1600°C and Cr-Fe-Si-C_{sat} (Cr/Fe=4.0 and 1.5) at 1550°C. Silicon activities were determined by measurement of partial pressures of SiO formed by the interaction of the melt with the material of the effusion cell. The mass-spectrometric method does not allow measurement of the carbon activity in the metal. For that reason carbon activities were calculated by use of known thermodynamic data and measured chromium and silicon activities.

INTRODUCTION

The commercial ferroalloys, high carbon ferrochromium and ferrochromium-silicide are best described by the Cr-Fe-Si-C system. The phase relations in the Cr-Si-C and Cr-Fe-Si-C systems with various Cr/Fe ratios have been determined in a previous investigation [4]. There is little information available on the component activities in this metal system. Most investigators just studied the carbon activity by different experimental methods [8-11] or by theoretical calculations [12]. These data show significant disagreement. Healy [2] calculated activities of the components in the Cr-Fe-C system based on the Cr-Fe-C phase diagram. Activities of silicon in Cr-Fe-Si-C alloys with various Cr/Fe ratios were determined in slag/metal/gas equilibrium experiments [7], but this was only for a very narrow interval of silicon concentrations. Also some preliminary calculations have been carried out for the Cr-Si-C_{sat} system [1].

The purpose of the present investigation is an experimental determination of the component activities in the Cr-Si-C and Cr-Fe-Si-C systems by using the mass spectrometric technique.

EXPERIMENTAL PROCEDURE

Samples for the present investigation were prepared from pure Cr, Fe, Si and Cr₃C₂ powders. Appropriate mixtures of these materials were heated up in alumina crucible to 1600°C in a resistance furnace with graphite heating element. The samples were kept in argon atmosphere for 0.5-2 hours and cooled down. The metal was separated from the crucible and crushed to a small size fraction before being heated up again and now kept at 1250°C in argon for 5 hours. Then the samples were crushed down once more and used for different types of analyses.

Experimental data were obtained by the Knudsen effusion method with mass spectral monitoring of the gas-phase composition on an MS-1301 mass spectrometer. Double effusion cells (Fig. 1) with sublimation-to-effusion area ratio ≥ 300 were used. The sample to be

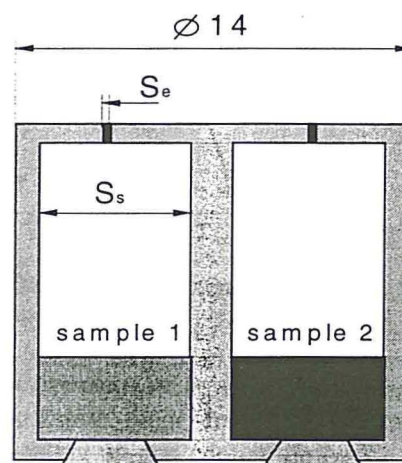


Fig.1. Double effusion cell.

S_e - effusion area

S_s - sublimation area

$S_s/S_e \geq 300$

investigated was placed in the first effusion cell and the standard sample with known activity of the studied element (or elements) - in the second cell. The temperature was measured with an optical EOP-66 pyrometer to better than ± 5 K. The known melting temperatures of Ag, Fe and Si were used for calibration of the pyrometer.

Initially, experiments were carried out with the binary systems Cr-Si and Cr-C. The purpose was to compare the obtained results with known literature data and by that to establish the reliability of the measuring method.

Cr-Si system

According to the research plan, 5 samples in the Cr-Si system were prepared for mass-spectrometric analysis:

Sample 1:	Cr-15 mol % Si
Sample 2:	Cr_3Si
Sample 3:	Cr_5Si_3
Sample 4:	Cr-56 mol % Si
Sample 5:	Cr-82 mol % Si.

These samples were examined in alumina effusion cells. Current intensities of the observed ions are given in Table 1 relative to I_{Cr^+} , where I_{Cr^+} is defined as 100. Seven mass-spectrometric experiments were conducted in this part of the investigation. The experimental scheme is given below:

Exp no.	1-st part of cell	2-nd part of cell
1	Cr	Cr_3Si
2	Cr_3Si	Sample 4
3	Sample 4	Sample 5
4	Sample 4	Sample 1
5	Cr	Sample 5
6	Sample 1	Cr_3Si
7	Cr	Cr_5Si_3

Cr-C system

Four samples were investigated in the Cr-C system:

Sample 1:	Cr_{23}C_6
Sample 2:	Cr_3C_2
Sample 3:	{0.864Cr+0.136C}
Sample 4:	{0.821Cr+0.179C}

Sample 3 corresponds to the composition of carbon saturated liquid at 1773 K and sample 4 to carbon saturated liquid at 1873 K.

The sublimation of the first two samples were carried out at 1500-1550 K. Comparison of the ionic current intensities in these experiments is given in Table 1. Furthermore, the samples {0.864Cr+0.136C} and {0.821Cr+0.179C} were evaporated from double alumina cells at 1800-1870 K and 1900-1950 K respectively. Pure chromium was used as the standard substance. The results of these investigations are given in the Tables 3 and 4.

Cr-Si-C_{sat} and Cr-Fe-Si-C_{sat} systems

Measurements were carried out with different metal samples belonging to the Cr-Si-C_{sat} and Cr-Fe-Si-C_{sat} systems. The Cr/Fe ratios for these experiments were 1.5 and 4. Zirconia effusion cells were used for these experiments. The planned measurements for the Cr-Si-C_{sat} system are shown in Fig.2. The metal compositions were chosen along a line of "carbon saturation" at 1873 K according to the Cr-Si-C phase diagram [4]. The lower ends of the arrows indicate the composition of the investigated samples, and the upper ends indicate the fact that these measurements were carried out at temperatures higher than the liquidus temperatures.

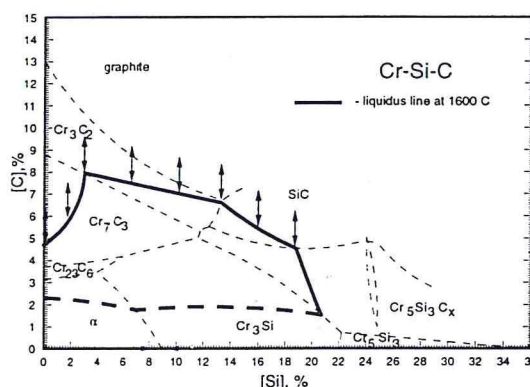


Fig.2. Plan of experiments in the Cr-Si-C system.

The measurements of P_{Cr} and P_{SiO} were made in the temperature range from 1873 to 2000 K during heating up and cooling down. Cr_3Si was always used as the standard (at 1900 K: $a_{\text{Cr}}=0.47$; $a_{\text{Si}}=0.028$ [14]).

Also in the Cr-Fe-Si-C_{sat} quaternary system, the investigated compositions were chosen along a line of "carbon saturation" at 1823 K according to the Cr-Fe-Si-C (Cr/Fe=4 and 1.5) phase diagrams [4]. The measurements of P_{Cr} , P_{Fe} and P_{SiO} were made in the temperature range 1823-1870 K. Pure Cr, Fe, and Si were first used as standards for a sample containing 4% Si and 7.3% C with Cr/Fe=4 (*sample A*). *Sample A* was next used as standard for *sample B* (Si=0%, C=4.8%, Cr/Fe=4) and for *sample C* (Si=20%, C=2.9%, Cr/Fe=4). *Sample C* was selected as the standard for the rest of the samples. Obtained components activities refer to $Cr_{(s)}$, $Fe_{(l)}$, $Si_{(l)}$ and $C_{(graph.)}$.

EXPERIMENTAL RESULTS AND DISCUSSION

Cr-Si system

Some experimental results for the binary Cr-Si system are presented in Fig.3, showing the relation: $\lg(I_{Cr} \cdot T) = f(1/T)$. From these data the enthalpy of chromium sublimation can be calculated according to the 2nd and 3rd thermodynamic laws. Analysis of our experimental results for pure chromium indicates that the obtained enthalpy of sublimation always was below the previously reported value [14] by 4-13 kJ/mole. To avoid systematic errors, the results of the mass-spectrometric measurements were calibrated based on the enthalpy of sublimation of pure chromium. This was done by adding the mentioned difference to the value of chromium sublimation for the different samples.

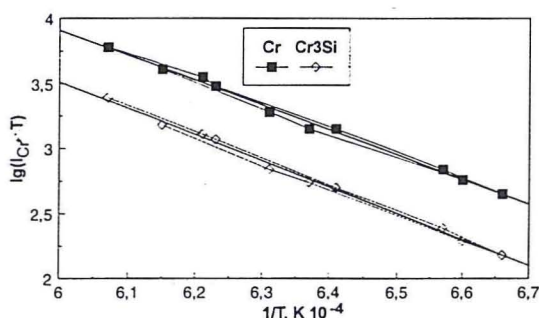
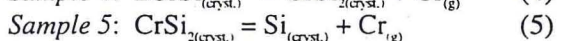
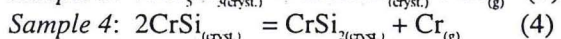
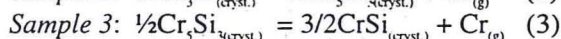
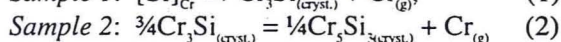
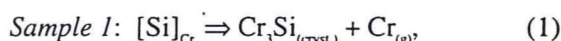


Fig.3. An example of experimental results for the Cr-Si system.

The sublimation enthalpy of Cr obtained from the experiments for reactions (2) and (3), shown in Table 2, is a proof of the equilibrium character of the effusion runs, and also indicates that the effusion cell material (Al_2O_3) is sufficiently inert to the investigated samples in the given temperature range. This is supported by the fact that our experimental enthalpies of sublimation are close to the known literature data obtained by different methods.

The determination of all component activities in one test is basically possible. In our case the transfer of silicon into the gas phase was realized by partial interaction of silicon in the sample with the cell material. Analysis of the mass spectra of the saturated vapours over chromium carbides and silicides (Table 1) indicate that the effusion cell material (Al_2O_3) reacts slightly with the components of the investigated samples. This is confirmed by the occurrence of SiO^+ , CO^+ and small amounts of Al^+ and Al_2O^+ ions in the mass-spectra.

The sublimation process of the investigated samples is described by the following reactions:



$[Si]_{Cr}$ is solid solution of silicon in chromium.

Then the activity of chromium can easily be calculated:

$$a_{Cr(2)} = \frac{I_{Cr^{+}(2)}}{I_{Cr^{+}(1)}} \cdot a_{Cr(1)} \quad (6)$$

Where:

$a_{Cr(1)}$ is the activity of chromium in a standard sample. In experiment No 1 the standard sample was pure chromium, and the sublimation process is described by the reaction: $Cr = Cr_{(g)}$.

$a_{Cr(2)}$ is the activity of a chromium in an investigated sample.

$I_{Cr+(1)}$ and $I_{Cr+(2)}$ are intensities of ionic currents of chromium above standard and investigated samples, respectively.

Table 1. Mass spectra of saturated vapours ($U_{\text{ionization}}=20 \text{ eV}$)

Composition	SiO ⁺	CO ⁺	Al ⁺	Al ₂ O ⁺	Cr ⁺	T, K
Cr ₃ Si	1,2	—	1,0	1,5	100 [*]	1500
Cr ₅ Si ₃	44,3	—	1,0	2,0	100	1500
Cr ₂₃ C ₆	—	18	0,6	2,0	100 ^{**}	1550
Cr ₃ C ₂	—	160	2,0	5,0	100	1550

$$I_{\text{Cr}^+[\text{Cr}_3\text{Si}]} / I_{\text{Cr}^+[\text{Cr}_5\text{Si}_3]} = 4,1 \pm 0,1;$$

$$I_{\text{Cr}^+[\text{Cr}_{23}\text{C}_6]} / I_{\text{Cr}^+[\text{Cr}_3\text{C}_2]} = 9,0 \pm 0,5$$

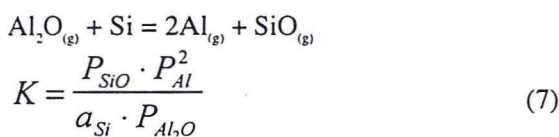
Table 2. Enthalpy of chromium sublimation, kJ/mole

reaction	$a_{\text{Cr}}(1500 \text{ K})$	$\Delta H^0(\text{Cr}, T \text{ K})$		T, K	reference
		(II) [*]	(III) ^{**}		
$3/4\text{Cr}_3\text{Si}_{(\text{cryst.})} = 1/4\text{Cr}_5\text{Si}_{3(\text{cryst.})} + \text{Cr}_{(\text{g})}$ (2)	0.35	398±5	401±3	1400-1550	this work
	0.30	403		1500	[14]
	0.38	385		1500	[14a]
$1/2\text{Cr}_5\text{Si}_{3(\text{cryst.})} = 3/2\text{CrSi}_{(\text{cryst.})} + \text{Cr}_{(\text{g})}$ (3)	0.085	402±8	403±3	1400-1550	this work
	0.076	407		1500	[14]
	0.010	441		1500	[14a]

* calculated from the "second law" using experimental dependencies: $\ln(p_{\text{Cr}})=f(1/T)$ or $\ln(I_{\text{Cr}}^+T)=f(1/T)$

** calculated from the "third law" using experimental data for the value of chromium vapour pressure and literature data [14] for the entropy of reaction.

As already mentioned, the samples reacted slightly with the material of the cell. This interaction between silicon in the metal and alumina can be described by the reaction:



Then the activity of silicon can then be calculated from the equation:

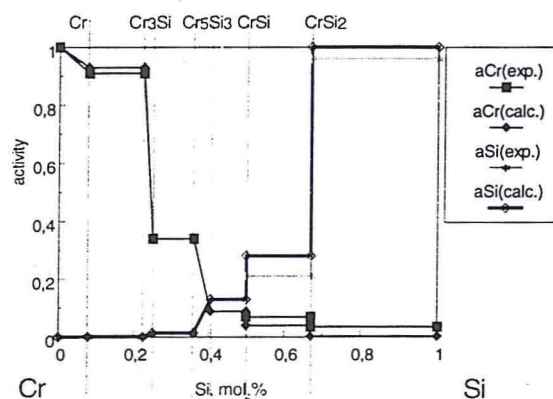
$$a_{\text{Si}(2)} = \frac{I_{\text{SiO}^+(2)}}{I_{\text{SiO}^+(1)}} \cdot a_{\text{Si}(1)} \cdot \frac{I_{\text{Al}^+(2)}^2 \cdot I_{\text{Al}_2\text{O}^+(1)}}{I_{\text{Al}^+(1)}^2 \cdot I_{\text{Al}_2\text{O}^+(2)}} \quad (8)$$

Where,

$a_{\text{Si}(1)}$ and $a_{\text{Si}(2)}$ are activities of silicon in a standard and an investigated sample;

$I_{\text{SiO}^+(1)}$, $I_{\text{Al}^+(1)}$ and $I_{\text{Al}_2\text{O}^+(1)}$ are intensities of SiO⁺, Al⁺ and Al₂O⁺ ionic currents above a standard sample;

$I_{\text{SiO}^+(2)}$, $I_{\text{Al}^+(2)}$ and $I_{\text{Al}_2\text{O}^+(2)}$ are intensities of SiO⁺, Al⁺ and Al₂O⁺ ionic currents above an investigated sample.

**Fig.4.** Component activities in the Cr-Si system at 1600 K.

The measured activities of chromium and silicon in the Cr-Si system at 1600 K are shown in Fig.4. Experimental values show good agreement with calculated values.

Thus, the introduction of Al₂O₃ seems to be without noticeable effect on the thermodynamics of the investigated system. So far measurements of SiO⁺, Al⁺ and Al₂O⁺ ionic currents make it possible to determine the

Table 3. Thermodynamic characteristics of vaporisation processes of samples {xCr+(1-x)C}

x	a_{Cr}	γ_{Cr}	$\Delta_v H^0(Cr, T)$	$\lg P_{Cr}(\text{mm Hg})=f(1/T)$	T, K
1.0	1.0	1.0	374 [7] 351 [7]	$\lg P(Cr_{(s)})=-19540/T+9.70$ $\lg P(Cr_{(m)})=-18340/T+9.13$	1700÷1900 ≥2130
0.864	0.82±0.02	0.94±0.02	354.5±2.1	$\lg P=-18530/T+9.14$	1800-1870
0.821	0.74±0.02	0.90±0.02	356.1±2.4	$\lg P=-18620/T+9.12$	1900-1950

Table 4. Component activities in {xCr+(1-x)C} system

X_{Cr}	X_C	T, K	a_{Cr}	a_C	ref.
0.864	0.136	1773	0.82	0.0035	this work
0.821	0.179	1873	0.74	0.0087	this work
			0.56	0.017	[8]
			0.65	0.01	[9]

silicon activity. However, as the determination of the silicon activity requires measurement of six different values (of which two are in square power), the error of obtained value can increase dramatically. For example, we obtained silicon activities equal to $6 \cdot 10^{-4}$ and $1 \cdot 10^{-3}$ for exactly the same sample (No.1) in different experiments. For that reason it could be better to use only the partial pressures of SiO for approximate determination of silicon activities. This is quite reasonable if investigated and standard samples have approximately similar chemical composition. Then:

$$\frac{I_{Al^{+}(2)}^2 \cdot I_{Al_2O^{+}(1)}}{I_{Al^{+}(1)}^2 \cdot I_{Al_2O^{+}(2)}} \approx 1 \quad (9)$$

This conclusion can be confirmed by the measured silicon activity ratio for Cr_3Si and Cr_5Si_3 , being $a_{Si(Cr_5Si_3)}/a_{Si(Cr_3Si)}=9.0 \pm 1.5$ (Table 1). This value agrees well with the literature data: 9.82 [14]. Therefore, to determine the silicon activity in the chromium silicides it seems sufficient to measure the SiO^{+} ion current in each compartment of the double cell.

Cr-C system

The sublimation processes can be described by the following reactions:

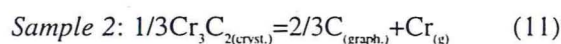
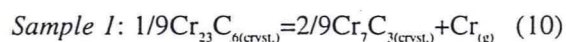


Table 1 shows that the content of CO^{+} ions in the mass spectra of saturated gases is not proportional to the carbon activity in the chromium carbides, and unlike in the Cr-Si system we did not obtain an unambiguous correlation. This is presumably associated with difficulties of measuring mass spectral lines of gases (CO) as compared to those of vapour components (Cr or SiO).

Nevertheless, in spite of the difficulties of experimental determination of carbon activity in the melt, it can be calculated from the measured chromium or silicon activity if the thermodynamic properties of corresponding carbides are known. As an example for chromium carbide formation:



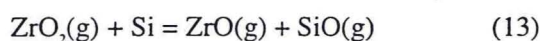
$$K = \frac{a_{Cr_xC_y}}{a_{Cr}^x \cdot a_C^y} \text{ or } a_C^y = \frac{a_{Cr_xC_y}}{a_{Cr}^x \cdot K}$$

The observed chromium activities in samples {0.864Cr+0.136C} and {0.821Cr+0.179C} are given in Table 3. Here data for vaporisation of pure chromium from $Cr_{(s)}$ and $Cr_{(m)}$ were taken from the literature [14]. According to the Cr-C binary phase diagram [3], the sample {0.864Cr+0.136C} is in equilibrium with $Cr_{23}C_6$ at 1773 K ($K_{p(1773K)}=3.885 \cdot 10^{14}$). The sample {0.821Cr+0.179C} is in equilibrium with Cr_7C_3 at 1873 K ($K_{p(1873K)}=4.694 \cdot 10^6$). Then the carbon activity can be calculated from reaction (12). The results of the calculations are shown in Table 4. They are in satisfactory agreement with previously reported data [1, 2].

Cr-Si-C_{sat} and Cr-Fe-Si-C_{sat} systems

The activities of chromium, silicon, carbon, and iron in the investigated alloys are shown as functions of the silicon concentration in the Figures 5-8. The activities of chromium and iron were calculated as in equation (6).

As mentioned, zirconium effusion cells were used in these experiments. Equilibrium in the zirconia cell is described by the reaction:



As the values of P_{ZrO_2} and P_{ZrO} were below the sensitivity of our apparatus, the silicon activity in the metal was here, as for the experiments in the alumina cells, calculated from the measured ratios of P_{SiO} from both parts of the double cell.

The activity of carbon in iron-free Cr-Si-C_{sat} alloys is calculated based on equilibrium between molten alloys and chromium carbides or silicon carbide according to the Cr-Si-C phase diagram [4]. Thermodynamic data for the chromium carbides are taken from [14] and for silicon carbide from [5]. The carbon activity in the silicon-free alloy is very low, only $a_c=0.0087$ at 1873 K. For the same alloy $a_c=0.74$.

The carbon activities in Cr-Fe-Si-C_{sat} alloys are calculated from established equilibrium with graphite ($a_c=1$) and with silicon carbide (Fig. 7). In the lower silicon range the carbon saturated alloys are equilibrated with chromium/iron carbides having a complex chemical composition - M_xC_y , where $M=\text{Cr}+\text{Fe}$. Thermodynamic data for formation of such carbides are not available in the literature.

The chromium activity in the silicon-free Cr-Fe-C_{sat} alloy, is $a_{\text{Cr}}=0.368$ (Cr/Fe=4) and $a_{\text{Cr}}=0.207$ (Cr/Fe=1.5) at 1823 K. The activity relations in this system is influenced by the formation of the stable carbides, M_xC_y .

The activity of carbon increases with increasing concentration of silicon in the Cr-Fe-Si-C_{sat} melt, and reaches its maximum value ($a_c=1$) where equilibrium with graphite is established.

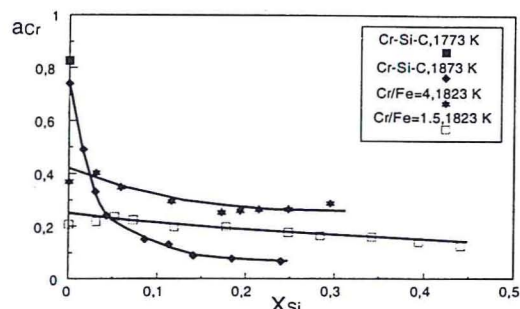


Fig.5. Chromium activity in Cr-Fe-Si-C_{sat} alloys with different Cr/Fe ratios.

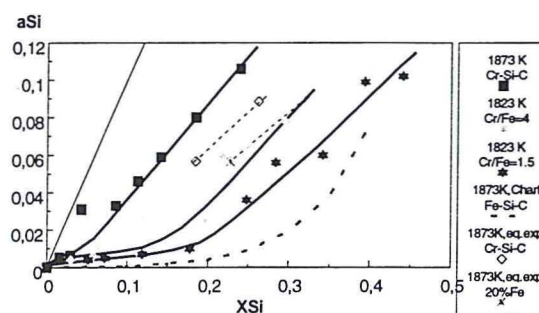


Fig.6. Silicon activity in Cr-Fe-Si-C_{sat} alloys with different Cr/Fe ratios.

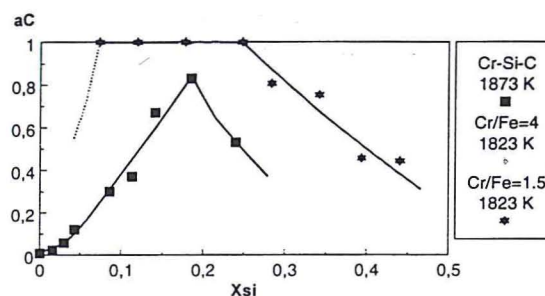


Fig.7. Carbon activity in Cr-Fe-Si-C_{sat} alloys with different Cr/Fe ratios.

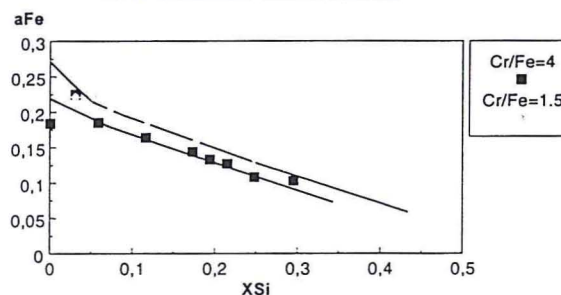


Fig.8. Iron activity in Cr-Fe-Si-C_{sat} alloys with different Cr/Fe ratios at 1823 K.

In the Cr-Si-C system, equilibrium with graphite is not reached. The maximum carbon activity is $a_C=0.83$ at 1873 K in the Cr_3C_2/SiC coexistence point. At the same time, the activity of chromium decreases and the activity of silicon increases with increasing X_{Si} . From Fig. 6 and 7 it can be seen that decreasing Cr/Fe ratios result in decreasing silicon activity and an extension of the range of Si concentrations where equilibrium with graphite is established. Fig. 6 compares the present silicon activities with data from Chart [6] for the Fe-Si-C system and with the results from metal/slag/gas equilibrium experiments [7]. In spite of some disagreement between the experimental data obtained by various methods for the Cr-Si-C system, it can be indicated that they describe the investigated systems reasonably well.

The dependence of the chromium activity on the Cr/Fe ratio has a more complex character (Fig. 5). In the lowest range of silicon concentrations, the activity of chromium increases as expected with increasing Cr/Fe ratio and reaches its maximum value in the iron-free Cr-Si-C alloy. However, the activity of chromium in the iron-free system decreases much faster than in alloys with iron when the silicon concentration is increased. This is probably connected to the differences of components interaction with iron and with chromium.

The activity of iron in liquid Cr-Fe-Si-C_{sat} alloys decreases with increasing silicon contents and naturally also with increasing Cr/Fe ratio, see Fig. 8.

CONCLUSIONS

1. It has been shown that the mass-spectrometric method can be used for thermodynamic investigation of metallic systems. Component activities can be measured directly as for Cr and Fe. Si activities can be measured indirectly.

2. Activities of chromium and iron were determined by mass-spectrometric measurements for the following systems: Cr-Si-C_{sat} at 1600°C and Cr-Fe-Si-C_{sat} (Cr/Fe=4.0 and 1.5) at 1550°C.

3. Silicon activities were determined by measurement of SiO partial pressures. SiO is formed by the interaction of the melts with the effusion cell material. These measurements are probably not very accurate. As it was shown, in addition to the SiO partial pressure, it is also necessary to measure the P_{Al} and P_{Al_2O} to determine the absolute values of the silicon activities.

4. The mass-spectrometric method does not allow measurement of the carbon activities in the metal. This activity has been calculated from the experimental results of chromium and silicon activities combined with use of known thermodynamic data for corresponding carbides.

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