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# SILICON AND CARBON IN CHROMIUM ALLOYS

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## ABSTRACT

A phase diagram has been constructed for the Cr-Fe-Si-$C_{sat}$ system at 1600°C based on measured carbon solubilities, metallographic observations and published data.

Further, liquid slags in the $SiO_2$-MgO-$Al_2O_3$ system have been equilibrated with Cr-Fe-Si-$C_{sat}$ alloys in graphite crucibles at 1600°C in CO atmosphere, and the distribution of silicon between slag and metal was determined. Slag and metal established equilibrium with SiC at the existing conditions. The silicon content depends on the silica activity of the slag and on the iron content of the metal, increasing e.g. from 18.5% Si in Cr-Si-$C_{sat}$ to 25.6% Si in Fe-Cr(5%)-Si-$C_{sat}$, both alloys in equilibrium with silica saturated slags. The results are shown graphically in the slag phase diagram as lines of constant silicon content in the metal.

## INTRODUCTION

Carbon solubility in chromium rich Cr-Fe-Si-C alloys has been studied by many scientists, but so far only the base system, Cr-Fe-C, has been carefully investigated [1]. Only limited experimental data are available in the literature about the influence of silicon on carbon solubility in the metal system, especially for alloys with low contents of silicon (Si≤3%).

Measurements of equilibrium between $SiO_2$-MgO-$Al_2O_3$ slags and Cr-Fe-Si-C alloys have not been reported in the literature. Rein and Chipman [2] studied equilibrium relations between this slag system and Fe-Si-C alloys. Eric and Akyüzlü [3] determined the distribution of silicon and chromium between carbon-saturated Cr-Fe-Si-C alloys and slags with about 35% CaO.

In the following, carbon solubility and phase relations in Cr-Fe-Si-C alloys with different Cr/Fe ratios will be discussed at first. Next results from studies of equilibrium between $SiO_2$-MgO-$Al_2O_3$ slags and Cr-Fe-Si-C alloys are presented and discussed.

## EXPERIMENTAL

Carbon solubility experiments

The studies of carbon solubility and phase relations in Cr-Si-C and Cr-Fe-Si-C alloys (Cr/Fe=4; 1.5; 0.25) were carried out in a resistance furnace with graphite heating element at 1600°C in Ar atmosphere. 100g mixture of pure Cr, Fe and C powders in appropriate amounts were placed in a graphite crucible and kept under specified conditions for 1 hour, which was sufficient to reach carbon saturation. Samples of the metal were taken by suction into silica tubes with pinhole having a diameter of about 1 mm. After the first sampling, a certain amount of additional silicon was added, and after 30 minutes a second sample was taken and so on. In the silicon rich area, samples were taken every 15 minutes. The samples of metal were analyzed on carbon and silicon. Further, the structure of some metal samples and crucible/metal interfaces were investigated by electron microprobe analysis.

Metal/slag/gas equilibrium

The equilibrium experiments were also carried out in a resistance furnace with graphite heating element at 1600°C. The temperature was measured with a Pt/Pt-10%Rh thermocouple close to the bottom of the crucible. During heating up, the atmosphere was changed from Ar to CO at 1300°C and the CO atmosphere was kept until the end of the test.

The initial metal compositions were prepared by mixing pure chromium, iron, silicon and carbon powders in certain proportions. The range of initial alloy compositions were as follows:

| | |
|---|---|
| Carbon | : 1-5 % |
| Silicon | : 14-28 % |
| Iron | : 20 % (tests were also made with 0, 50 and 70% Fe) |
| Chromium | : balance |

The slags were prepared as mixtures of a master slag and pure oxide components. The range of initial slag compositions was 50-75% $SiO_2$ with fixed magnesia to alumina ratios (M/A=0.5; 1.0; 1.5; 2.0).

About 3g of metal and 4g of slag were placed in the crucible and kept at chosen conditions (T=1600°C; $P_{CO}$=1 atm) for 24 hours. Then the crucible with alloy and slag was pulled up to the cooling jacket for quenching. Metal and slag were carefully separated from each other and from crucible contamination and analyzed. In addition to wet chemical analysis, slag samples were also analyzed by electron microprobe analysis. The different methods were in good agreement except that wet chemical analysis gave a higher content of $Cr_2O_3$ which is believed caused by small metallic particles in the slag.

Two types of crucibles were used in the present investigation. Graphite crucibles with an inside quartz lining were used for determination of metal/slag/gas equilibria with silica saturated slags. In these cases 25g of metal and 5g of slag were equilibrated. In other cases ordinary graphite crucibles were used.

## RESULTS AND DISCUSSION

Carbon solubility experiment

Measured silicon-carbon relations in Cr-Fe-Si-C alloys with different Cr/Fe ratios are presented in Fig.1.

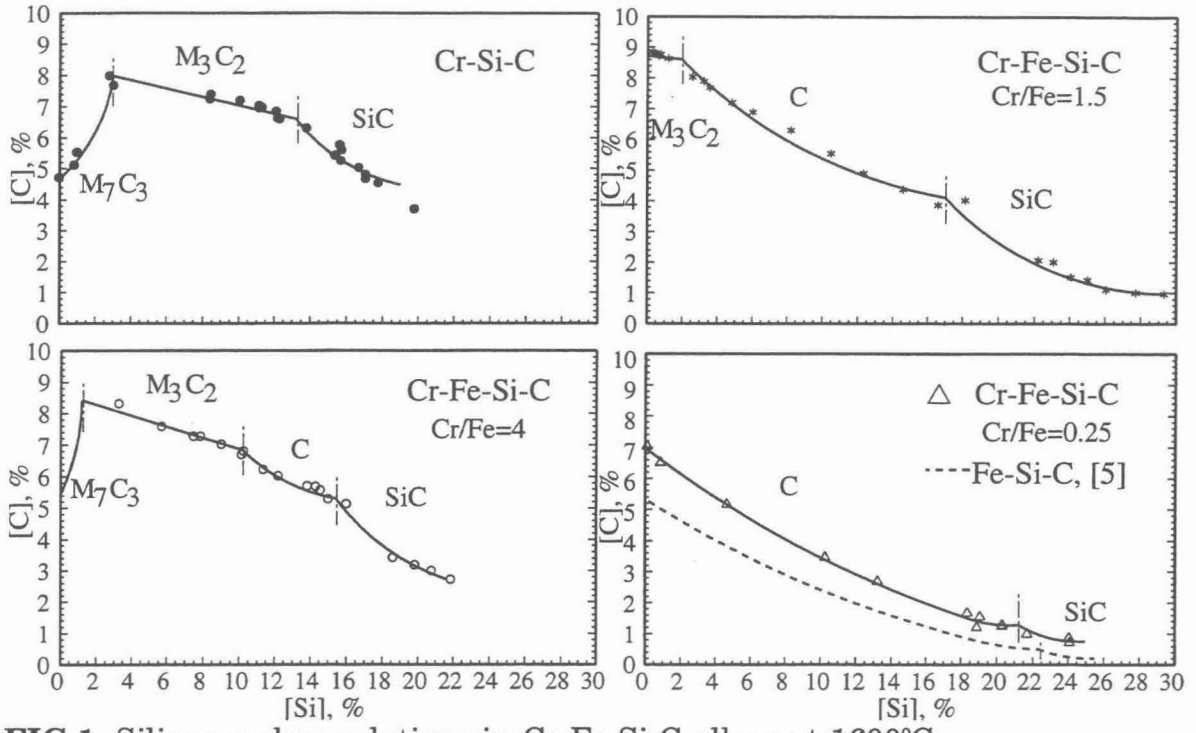


**FIG.1.** Silicon-carbon relations in Cr-Fe-Si-C alloys at 1600°C.

For chromium rich alloys, the carbon content increases initially with increasing silicon content in the metal. After a certain "critical" value is reached, the carbon content decreases with further increasing content of silicon. The carbon contents in silicon-free alloys are in a good agreement with the Cr-C phase diagram reported by Hansen [4], and with carbon solubility data in the Cr-Fe-C system reported by Griffing and Healy [1].

The solubility curve representing iron-free Cr-Si-C alloys shows two breaks, dividing the system into three areas. Study of the metal and the crucible/metal interface in the electron microscope shows that :

- in the first area, where carbon is increasing with increasing silicon content, the primary crystals in the metal are $Cr_7C_3$. Between the graphite crucible and liquid metal there are two types of carbide: close to the graphite - $Cr_3C_2$ and close to the metal - $Cr_7C_3$;

- in the next area the primary crystals are $Cr_3C_2$. Between graphite and metal only the carbide $Cr_3C_2$ was found.

- in the third area SiC is formed between the graphite crucible and metal.

Thus, for the Cr-Si-C system, the stable carbide phases are with increasing silicon content: $Cr_7C_3$ in the first; $Cr_3C_2$ in the second and SiC in the third area.

For alloys with Cr/Fe=4 there seems to be a fourth area between 10 and 15.5% Si. Metallographic observations indicates absence of any additional carbide phase between the graphite crucible and the metal in this area. This means that graphite is a stable phase between the $M_3C_2$ (M=Cr+Fe) and SiC stability areas.

Further, there is no area of $M_7C_3$ stability in alloys with Cr/Fe=1.5 and there is no area of $M_3C_2$ stability with Cr/Fe ratio less than approximately 1.2.

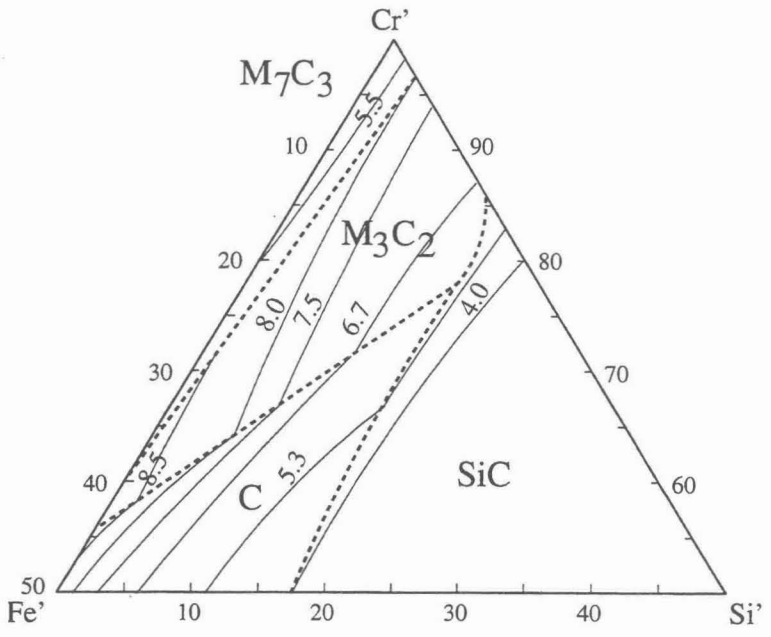


**FIG.2.** Cr-Fe-Si-$C_{sat}$ system. Sketched phase diagram at 1600 °C. Carbon saturation contents are indicated (wt.%).
LEGEND:
Cr'=100[Cr]/(100-[C]);
Fe'=100[Fe]/(100-[C]);
Si'=100[Si]/(100-[C])

The resulting phase diagram of the Cr-Fe-Si-$C_{sat}$ system and lines of iso-carbon concentrations at 1600°C are sketched in Fig.2, projected from the carbon corner to the Cr-Fe-Si triangle. For simplicity, in this paper the symbol $C_{sat}$ is used for all carbon saturated melts, regardless of whether the coexisting phase is graphite or some carbide. The given carbon concentrations are in a good agreement with data published by other investigators [1, 5, 6]. The "critical" silicon contents where metal are in equilibrium with graphite and SiC, are also in satisfactory agreement with results reported by others [6, 7].

Metal/slag/gas equilibrium

Slags for high carbon ferrochromium and ferrosilicochromium production are best described by the $SiO_2$-MgO-$Al_2O_3$-$Cr_2O_3$ system. However, after preliminary experiments, it was concluded that the equilibrium concentration of $Cr_2O_3$ in the slag is very low - less than 0.5 %. Therefore it seems safe to assume that chromium oxide does not have any considerable influence on the slag system.

The distribution of silicon between slag and metal is of considerable interest when studying equilibrium relations in the metal/slag/gas system. Reduction of $SiO_2$ from the slag, when graphite is the stable coexisting phase, can be described by the following reaction:

$$(SiO_2) + 2C_{gr.} = Si_{(l)} + 2CO \qquad (1)$$

At 1600°C [8]:

$$K_1 = \frac{P_{CO}^{\,2} \cdot a_{Si}}{a_{SiO2} \cdot a_C^{\,2}} = 0.22 \qquad \text{(where } a_C=1 \text{ for graphite saturation)}$$

At higher silicon contents, where SiC is the stable phase, the silica reduction proceeds according to the reaction:

$$(SiO_2) + 2SiC = 3Si_{(l)} + 2CO \qquad (2)$$

At 1600°C [8]:

$$K_2 = \frac{P_{CO}^{\,2} \cdot a_{Si}^{\,3}}{a_{SiO2} \cdot a_{SiC}^{\,2}} = 6.94 \cdot 10^{-4} \qquad \text{(where } a_{SiC}=1 \text{ for SiC saturation)}$$

The silicon content of the metal is a function of the silica content of the slag when complete equilibrium is established, and the silicon distribution between slag and metal depends on the CO pressure. The partial pressure of $SiO_{(g)}$ is quite low at 1600°C and hence the CO pressure is close to 1 atm.

From the equations (1) and (2), it follows that metal and slag can coexist with SiC and graphite only at a certain silica activity in the slag and silicon activity in the metal, being at 1600°C and $P_{CO}$=1 atm:

$$a_{SiO2} = 0.26$$
$$a_{Si} = 0.0565$$

Fortunately, information is available about silica activities in the $SiO_2$-MgO-$Al_2O_3$ slag system [8]. According to Rein and Chipman, silica activities in the liquid slag area at 1600°C are always higher than 0.26, increasing from 0.3 to 1 with increasing silica content. Hence, at this temperature and for $P_{CO}$=1 atm, slag and metal must be in equilibrium with SiC, and equilibrium conditions are described by equation (2).

Experimental results are shown as solid curves in Fig.3 for slags with different magnesia to alumina weight ratios (M/A) in equilibrium with Cr-Fe(20%)-Si-$C_{sat}$ alloys. The liquid range for each M/A ratio is read from the $SiO_2$-MgO-$Al_2O_3$ phase diagram [9]. Only one experiment was carried out with silica saturated slag. The resulting alloy composition represent the end point for all the solid curves.

Several experiments were also carried out with Cr-Si-$C_{sat}$ alloys and slags with M/A=1. The results of these experiments are presented as open circles and the dashed curve in Fig.3. Silicon transfer between slag and metal is a slow process and equilibrium is not always reached even after 24 hours. The curves in Fig.3 are based on approach to equilibrium from both directions.

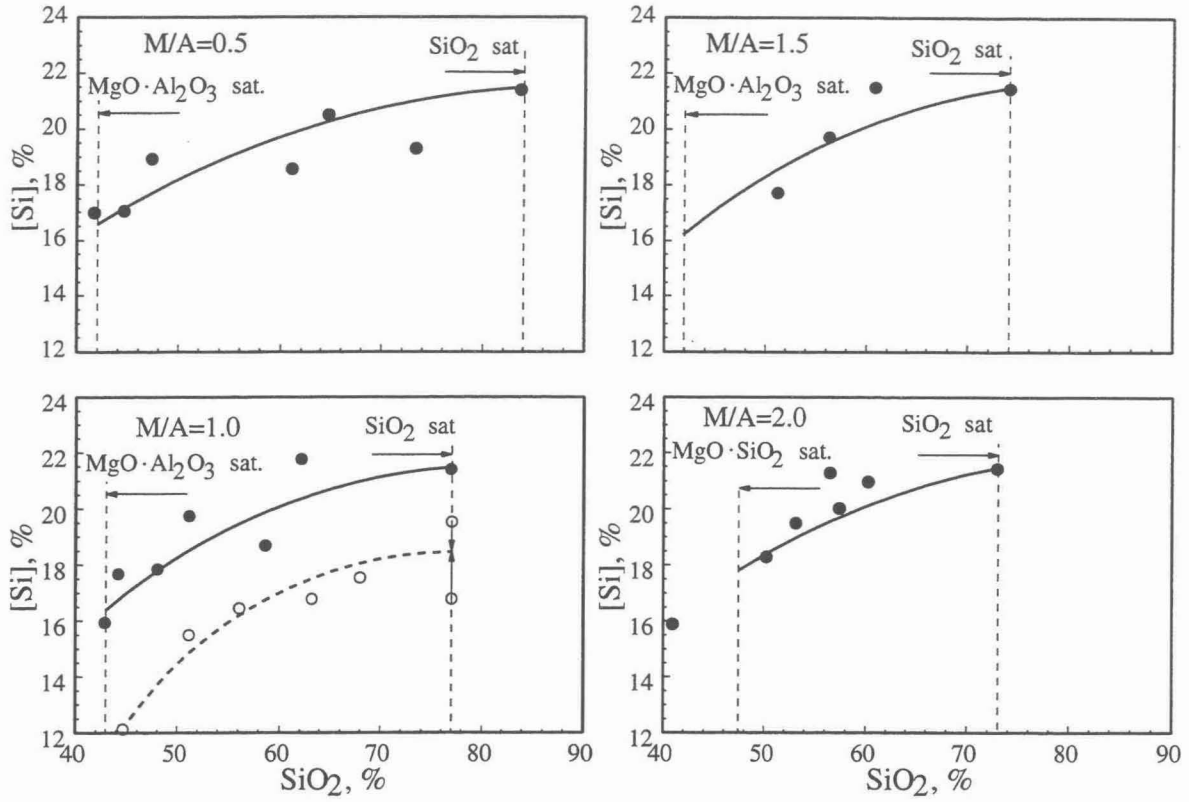


**FIG.3.** Equilibrium contents of Si in Cr-Fe(20%)-Si-$C_{sat}$ (solid curves) and Cr-Si-$C_{sat}$ (dashed curve) alloys at 1600°C in CO. Slag system $SiO_2$-MgO-$Al_2O_3$. Different M/A ratios.

Corresponding contents of Si and C in Cr-Fe(20%)-Si-$C_{sat}$ alloys at 1600°C are plotted in Fig.4.

Fig.5 shows iso-activity curves for silica [8] with corresponding silicon contents in equilibrated Cr-Fe(20%)-Si-$C_{sat}$ alloys. The equilibrium contents of silicon were obtained by interpolations from Fig.3, and is shown to increase from 17.3% to 21.5% with increasing silica in the slag from about 45% $SiO_2$ to silica saturation.

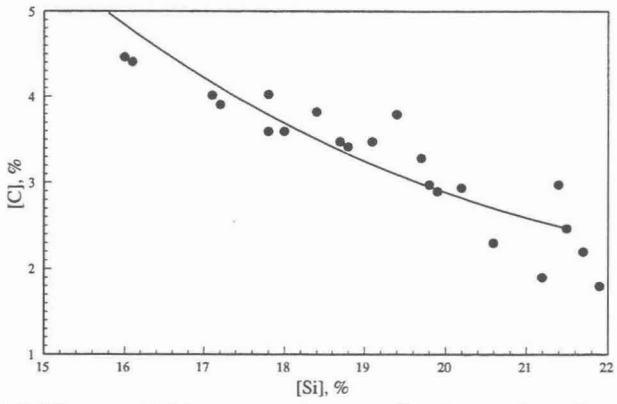


**FIG.4.** Silicon-carbon relations in Cr-Fe(20%)-Si-$C_{sat}$ alloys at 1600°C.

Silicon activities and activity coefficients are easily calculated when alloy compositions and corresponding silica activities are known. For each value of Si (Fig.5), the corresponding C content was read from the silicon-carbon relation curve in Fig.4. Knowing complete alloy compositions, the mole fractions of Si ($N_{Si}$) in the various Cr-Fe(20%)-Si-$C_{sat}$ alloys were calculated. The relation between $\log\gamma_{Si}$ and $N_{Si}$ shows a linear character in the investigated area of silicon concentrations and is described by the following correlation equation:

$$\log\gamma_{Si} = 0.444 \cdot N_{Si} - 0.706 \qquad (K_{cor.}=0.95) \qquad \textbf{(3)}$$

This relation is shown as line 4 in Fig.6. Line 1 is taken from Chart [11] and represents actually the Fe-Si system but may as well be said to represent the Fe-Si-$C_{sat}$ system in this range of silicon contents ($N_{Si}$>0.35) where the carbon contents ($N_C$<0.02) are of little influence [10].

A series of equilibrium measurements were also made with silica saturated slags and the following alloys: Cr-Si-$C_{sat}$, Cr-Fe(20%)-Si-$C_{sat}$, Fe-Cr(25%)-Si-$C_{sat}$ and Fe-Cr(5%)-Si-$C_{sat}$, all at 1600°C in presence of SiC and at $P_{CO}$=1 atm. The resulting carbon and silicon contents of the metal samples are shown in Table 1. As the activity of silica is unity, the activity of silicon is calculated to be: $a_{Si}$=0.0885 (eq.2). Activity coefficients were calculated and log$\gamma_{Si}$ values are given in the table.

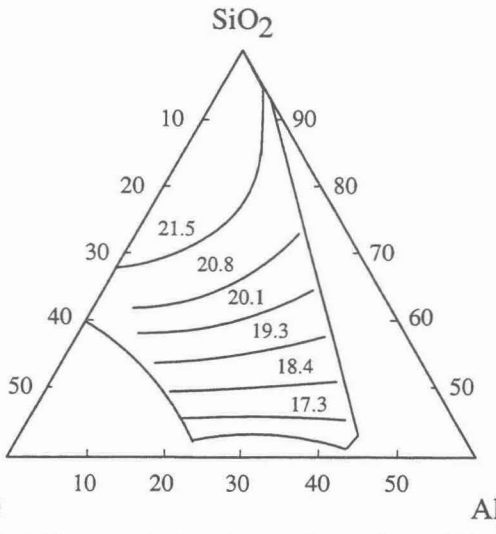


**FIG.5.** Iso-activity lines for silica [8] and corresponding Si contents in Cr-Fe(20%)-Si-$C_{sat}$ alloys in equilibrium with $SiO_2$-MgO-$Al_2O_3$ slags at 1600°C. Slag comp. in wt%.

'Critical' alloy compositions (C/SiC coexistence) at 1600°C were estimated based on Fig.1 and Fig.2 for the same alloy systems. These data are also shown in Table 1. As already discussed, the silicon activity in such alloys is at 1600°C: $a_{Si}$=0.0565. Corresponding activity coefficients were calculated and log$\gamma_{Si}$ values are given in the table.

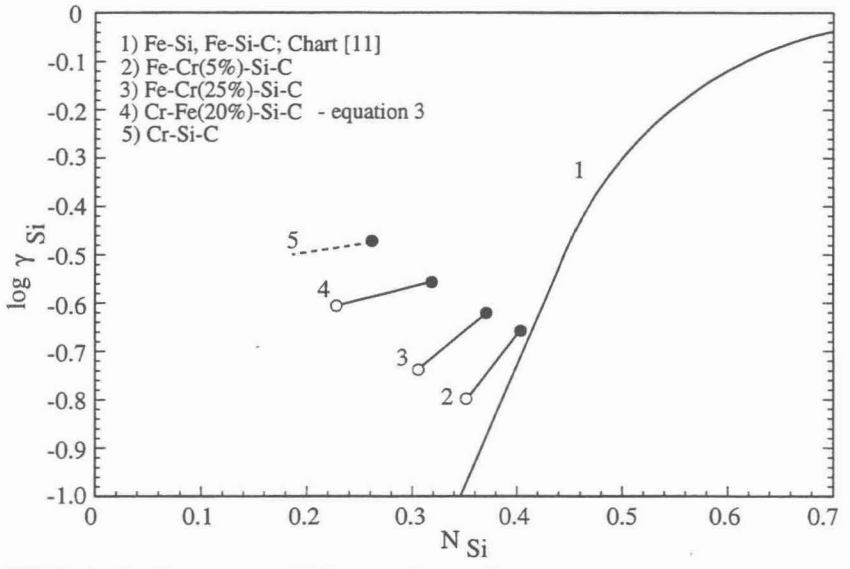


**FIG.6.** Influence of $N_{Si}$ on the silicon activity coefficient in Cr-Fe-Si-C system at 1600°C.

● - from $SiO_2$ saturation;

○ - from C-SiC coexistence.

**TABLE 1** *Corresponding C and Si contents of various alloy systems in equilibrium with SiC/C ('critical' values) and in equilibrium with silica saturated slags.*

| Alloy | 'Critical' alloy compositions (C/SiC) | | | Alloys in equilibrium with silica saturated slags. | | |
|---|---|---|---|---|---|---|
| | C % | Si % | $-\log\gamma_{Si}$ | C % | Si % | $-\log\gamma_{Si}$ |
| Fe-Cr(%5)-Si-$C_{sat}$ | 0.80 | 22.1 | 0.798 | 0.22 | 25.6 | 0.657 |
| Fe-Cr(25%)-Si-$C_{sat}$ | 2.10 | 19.8 | 0.738 | 0.94 | 24.0 | 0.620 |
| Cr-Fe(20%)-Si-$C_{sat}$ | 5.00 | 15.8 | 0.606 | 2.47 | 21.5 | 0.557 |
| Cr-Si-$C_{sat}$ | | | | 4.60 | 18.5 | 0.471 |

The lines 2-5 in Fig.6 show the relation between the silicon activity coefficients and $N_{Si}$ for the different Cr-Fe-Si-$C_{sat}$ alloy systems. The data are taken from Table 1. Results marked (o) represent 'critical' alloys, and results marked (•) represent alloys in equilibrium with silica saturated slags.

Information about silicon activities in the metal systems is very important because experimental investigations to determine equilibrium relations in the metal/slag/gas system are very time and labor consuming. Now it is possible to calculate the distribution of silicon between the present slag system and various Cr-Fe-Si-$C_{sat}$ alloys as well as between Cr-Fe-Si-$C_{sat}$ alloys and other slag systems

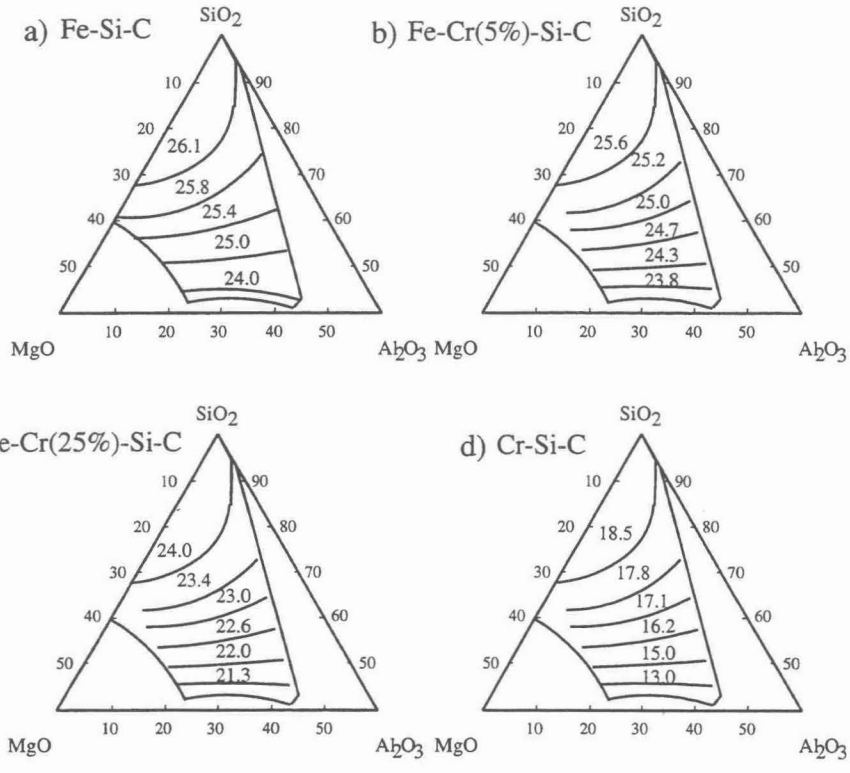


**FIG.7.** Distribution of silicon between Cr-Fe-Si-$C_{sat}$ alloys and $SiO_2$-MgO-$Al_2O_3$ slags at 1600°C in CO.

where the silica activities are well known. Such calculations have been carried out for the $SiO_2$-$MgO$-$Al_2O_3$ slag system and the different Cr-Fe-Si-$C_{sat}$ alloys at 1600°C in carbon monoxide atmosphere, and the results are presented in Fig.7. Picture **a),** gives the result of Rein and Chipman [2] for the Fe-Si-$C_{sat}$ system. The pictures **b)** and **c)** show calculated silicon contents in Fe-Cr(5%)-Si-$C_{sat}$ and Fe-Cr(25%)-Si-$C_{sat}$ alloys in equilibrium with $SiO_2$-$MgO$-$Al_2O_3$ slags. Picture **d)** for Cr-Si-$C_{sat}$ alloys is based on experimental data from Fig.3 (dashed curve).

We can concluded, that the distribution of silicon between slag and metal depends on the activity of silica in the slag and on the iron content in the alloy at given conditions. These effects are illustrated in Fig.8.

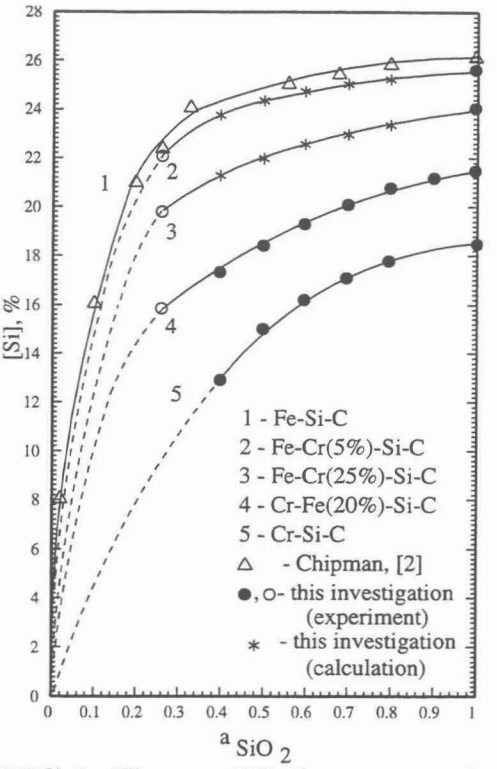


**FIG.8.** The equilibrium content of silicon for various Cr-Fe-Si-$C_{sat}$ alloys dependent on the silica activity in $SiO_2$-$MgO$-$Al_2O_3$ slags at 1600°C.

## CONCLUSIONS

A phase diagram has been developed for the Cr-Fe-Si-$C_{sat}$ system at 1600°C based on measured carbon solubilities, metallographic observations and published data.

Equilibrium between $SiO_2$-$MgO$-$Al_2O_3$ slags and Cr-Fe-Si-$C_{sat}$ alloys, in presence of SiC, have been studied at 1600°C in CO atmosphere. The silicon content of each alloy depends on the silica activity of the slag and on the iron content of the metal. The results are shown graphically as lines of constant silicon content of the metal in the slag phase diagram.

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## References

1. N.R.Griffing, W.D.Forgeng and G.W.Healy. "C-Cr-Fe liquidus surface", Trans.of AIME, v.224, 1962, pp.148-159.
2. Richard H. Rein and John Chipman. "The distribution of silicon between Fe-Si-C alloys and $SiO_2$-$CaO$-$MgO$-$Al_2O_3$ slags". Trans.of AIME, v.227, 1963, pp.1193-1203.

3. R.H.Eric and M.Akyüzlü. "Slag-metal equilibria in the system Fe-Cr-Si-C-Ca-Mg-Al-O", MINTEK report No M405, 1990.
4. M.Hansen. Constitution of Binary Alloys. McGraw-Hill Book Co, Second Ed., 1958.
5. J.Chipman, R.M.Alfred, L.W.Gott et al. "The solubility of carbon in molten iron and iron-silicon and iron-manganese alloys", Trans.of the A.S.M., v.44, 1952, pp.1215-1232.
6. Yu.A.Ageev, Yu.A.Danilovich et al. "Investigations of conditions for SiC formation and solubility of carbon in the Fe-Cr-Mn-Si system". Ferroalloys of chromium. Reports collection. Scientific-research institute of metallurgy. Moscow, 1986, pp.40-44.
7. A.M.Yanvarev, V.A.Rudenko et al. "About the interaction of SiC with iron and chromium". Izvestiya V.U.Z. Chernaya Metallurgiya. 1972, No 2, pp.75-78.
8. Richard H.Rein and John Chipman. "Activities in the liquid solution $SiO_2$-CaO-MgO-$Al_2O_3$ at 1600 °C". Trans.of AIME, v.233, 1965, pp.415-425.
9. E.M.Levin, C.R.Robbins, H.F.McMurdie. "Phase Diagrams for Ceramists", 1964.
10. John Chipman and Robert Baschwitz. "The activity of silicon in liquid Fe-Si-C alloys". Trans.of AIME, v.227, 1963, pp.473-478.
11. T.G.Chart. "A critical assessment of the thermodynamic properties of the system iron-silicon". High Temperature - High Pressure, v.2, 1970, pp.461-470.
12. Kossyrev K.L. and Olsen S.E. "Equilibrium in the production of ferrochromium". Sintef report STF24 F94713, Dec. 1994.