Equilibria Between Liquid Mn-Si Alloys and MnO-SiO₂-CaO-MgO Slags

G. J. W. KOR

The activity of silicon in manganese-silicon melts was determined at 1500°C. The results are in general agreement with the thermodynamic data of the iron-silicon system. Equilibria between manganese-silicon melts and slags containing MnO, SiO₂, CaO, and MgO were studied at 1400 and 1500°C in silica and magnesia crucibles. An empirical relationship easy to use in practice was derived, expressing the manganese and silicon distribution ratio between slag and metal as a function of the slag basicity. This relationship describes equilibria pertinent to the silicothermic reduction of manganese oxide and the production of silicomanganese. The present knowledge of the activities in the slag and metal phase is adequate to explain the experimental results. The presence of up to about 10 pct CaF₂ in the slag makes it possible to maintain a higher slag basicity and therefore a lower activity of silica, resulting in lower silicon contents in the metal. Iron contents of up to about 20 pct in the metal cause a slight increase in the silicon content of the metal under otherwise similar conditions. The effect of 1 to 2 pct carbon in the metal on the equilibrium was roughly estimated and found to be almost negligible.

Low or medium carbon ferromanganese is produced by reducing manganese oxide, usually in the form of high grade manganese ore, with the silicon contained in silicomanganese; this is the so-called silicothermic process. The principal chemical reaction is:

\[ 2\text{MnO}_x + x\text{Si} \text{ (in SiMn)} = 2\text{Mn} + x\text{SiO}_2. \]  

Lime is present in the slag to lower the activity of SiO₂ and increase that of MnO.

Because silicomanganese is expensive, it is advantageous to use MnO (\( x = 1 \)) as a reactant. For this case the equilibrium constant for Eq. [1] is:

\[ K_1 = \frac{a_{\text{Mn}}^2 \cdot a_{\text{SiO}_2}}{a_{\text{MnO}}^2 \cdot a_{\text{Si}}}. \]  

Knowledge of the activities of MnO and SiO₂ in the slag and of the activities of silicon and manganese in the metal phase is necessary to predict the compositions of slag and metal in equilibrium with each other.

In practice, the silicothermic reduction is done either in a tilting direct-act steel melting furnace or by a modified form of the so-called Perrin process, in which slag and metal phase are emulsified by a suitable technique. In either case, the duration of the refining period is determined by the time required to reach equilibrium.

Silicomanganese is produced by electric smelting of the proper amounts of manganese ore, silica, and coke in an electric furnace. Lime is usually present in the slags encountered in the production of silicomanganese. Hence, as in the silicothermic process, knowledge of the activities of MnO and SiO₂ in the slag as well as the activities of silicon and manganese in the metal is necessary to predict the compositions of slag and metal in equilibrium.

Little basic information is available on equilibria between Mn-Si melts and slags containing MnO, SiO₂, and CaO, with or without MgO. Tuset et al have studied equilibria between Mn-Si melts and MnO-SiO₂-CaO slags at 1530°C. However, as a consequence of the experimental technique used, Tuset et al were able to study only slags saturated with respect to SiO₂ or CaO-MnO solid solutions, and not containing MgO. Moreover, they restricted themselves to one temperature. The present work was undertaken to study slags containing MgO, more representative for those encountered in practice, and to include the effect of temperature on the equilibrium conditions.

**EXPERIMENTAL**

Manganese-silicon master alloys, containing various amounts of silicon, were prepared in a small vacuum furnace, using electrolytic manganese and 99.9 pct pure silicon as the starting materials. The master alloys were crushed and about 50 g of the crushed metal was used for each experiment. The slags were prepared by mixing the chemically pure dry constituents and pressing the mixture into small cylinders to facilitate charging.

Magnesia, silica, or manganese oxide crucibles were used; most experiments were done in MgO crucibles. The capacity of the crucibles was 50 g of metal and 50 g of slag, except for the MnO crucibles in which only about 4 g of metal and 4 g of slag could be charged.*

*A slag to metal weight ratio of about one is similar to that encountered in silicothermic reduction practice.

The MnO crucibles were made by pressing MnO powder into a cylinder, then drilling out the center, and sintering the crucible overnight in H₂ at about 1650°C. After this procedure the crucibles were dense and colored bright green.

The procedure for each experiment was as follows. The crucible, containing the metal, was lowered into the hot zone of a vertical molybdenum wound resistance furnace. The reaction tube was then closed and the temperature was gradually increased from about 600°C to the desired reaction temperature while argon...
RESULTS AND DISCUSSION

Activities in Mn-Si Melts

Thermodynamic data for the Mn-Si system have been reviewed by Chart. The activity of Mn in liquid Mn-Si alloys at 1800 K was determined by Gee and Rosenqvist who measured the vapor pressure of manganese by the transportation technique. Their data are in substantial agreement with the data of Ahmad and Pratt, who used a torsion effusion technique to measure the vapor pressure of manganese over Mn-Si melts. However, no experimental details are presented in the two Russian papers. In view of the generally good agreement between the work of Gee and Rosenqvist and Ahmad and Pratt, it was decided to use Gee and Rosenqvist's values for the activity of manganese in liquid Mn-Si alloys at 1520°C for subsequent calculations.

By means of a Gibbs-Duhem integration Gee and Rosenqvist obtained the activity of silicon in Mn-Si alloys at 1800 K. However, the authors pointed out that the accuracy in the activity coefficient of silicon is relatively small at silicon contents below about 5 pct. For instance, for an alloy containing 5 pct silicon the activity coefficient of silicon as calculated from the Gibbs-Duhem integration is about an order of magnitude lower than that derived from the equilibrium studies involving Mn-Si melts and MnO saturated manganese silicate slags.

To resolve this discrepancy it was decided to equilibrate Mn-Si melts with manganese silicate slags saturated with respect to either MnO or SiO2; the results of these experiments are summarized in Table I. By making use of the known activities in the MnO-SiO2 system at 1500°C and the activity of manganese in Mn-Si melts, the activity of silicon is calculated from Eq. [2] for which the value of the equilibrium constant is 330 at 1500°C. The derived values of log γSi are also listed in Table I.

<table>
<thead>
<tr>
<th>[pct Si]o</th>
<th>[pct Si]eq</th>
<th>NSi</th>
<th>[pct Cl]eq</th>
<th>aMn</th>
<th>Log γSi from Eq. [2]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>1.55</td>
<td>0.03</td>
<td></td>
<td>0.97</td>
<td>-2.18</td>
<td>equilibrium with slag for which aMnO = 1; aSiO2 = 0.07</td>
</tr>
<tr>
<td>2</td>
<td>1.40</td>
<td>0.027</td>
<td></td>
<td>0.973</td>
<td>-2.13</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.20</td>
<td>0.023</td>
<td></td>
<td>0.977</td>
<td>-2.06</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.40</td>
<td>0.027</td>
<td></td>
<td>0.973</td>
<td>-2.13</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>16.8</td>
<td>0.28</td>
<td></td>
<td>0.29</td>
<td>-1.60</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>17.3</td>
<td>0.29</td>
<td></td>
<td>0.275</td>
<td>-1.66</td>
<td></td>
</tr>
<tr>
<td>30.2*</td>
<td>0.46</td>
<td>0.27*</td>
<td></td>
<td>-1.34</td>
<td></td>
<td>equilibrium with graphite and β-SiC</td>
</tr>
</tbody>
</table>

Table I. Silicon Content of Mn-Si Melts in Equilibrium With Manganese Silicate Slags or Graphite and β-SiC at 1500°C

*average of four samples

To make use of the free energy of formation of Fe-Si at 1500°C, (-1.63 kcal) the activity of silicon in a Mn-Si-C melt (Neq = 0.01) is calculated as shown in Table I. Because the carbon content in this Mn-Si-C melt is low, the activity coefficient of silicon in this ternary melt is assumed to be approximately the same as in a binary carbon free melt. In fact, Chipman and Baschwitz have shown that log γSi in ternary Fe-Si-C melts is approximately the same function of NSi + NC as of NSi in binary Fe-Si melts, the approximation being better when the silicon content is high and the carbon content low. It is reasonable to assume that the same is true for manganese based melts.

The logarithm of the activity coefficient of silicon is plotted as a function on (1-NSi)2 in Fig. 1. For NSi \geq 0.45 (pct Si \leq 29.4) a linear relation is observed and log γSi is given by:

$$\log \gamma_{\text{Si}} = -1.17 (1-\text{NSi})^2 - 1.03 \quad [3]$$

valid at 1500°C. It is of interest to note that in the Fe-Si system log γSi is a linear function of (1-NSi)2 for NSi \leq 0.4.

The data obtained by Tuset et al. who equilibrated Mn-Si melts with manganese silicate slags saturated either with respect to MnO or SiO2 at 1530°C, are in good agreement with the present work, Fig. 1. Also