Slag-metal equilibrium in the production of low-carbon ferromanganese

by N. A. BARCZA*, Ph.D. (Wits.) (Member)

SYNOPSIS
An investigation was conducted into the reactions between the slag system MnO-CaO-MgO-SiO$_2$-(Al$_2$O$_3$) and the alloy system Mn-Fe-Si-(C). Synthetic slags representative of plant melts and a plant alloy were reacted in alumina crucibles at temperatures of 1400°C, 1450°C, 1500°C, and 1600°C. In similar experiments, slags were used that comprised a South African manganese ore with various amounts of lime and several synthetic alloys with various silicon contents and manganese-to-iron ratios. These experiments were conducted in a vertical molybdenum-wound resistance furnace with full temperature control. Slag-to-alloy ratios were also varied during the tests.

The rate of reduction of MnO and the MnO from the slag by the silicon in the alloy was extremely rapid, most of the reaction being completed within five minutes. The strongly exothermic nature of the reaction resulted in considerable generation of heat at the slag-alloy interface, causing convective stirring of the contents of the crucible and promoting the rate of reaction.

Equilibrium was usually attained after fifteen minutes. The major limitation governing the recovery of manganese is the need for the silicon content of the alloy to meet a maximum specification of 2 per cent. Higher concentrations of silicon in the final alloy of between 8 and 12 per cent favour good recoveries of manganese from the slag, but, since such an alloy is not salable, lower recoveries must apparently be tolerated. In alloys of 2 per cent silicon, low activities of the silicon are responsible for poor recoveries of manganese.

The activity of MnO in the slag can be increased by moderate additions of CaO and small amounts of MgO, i.e., by an increase in the basicity of the slag.

SAMEVATTING
Daar is ondersoek ingestel na die reaksies tussen die slakstelsel MnO-CaO-MgO-SiO$_2$-(Al$_2$O$_3$) en die legeringstelsel Mn-Fe-Si-(C). Sintetiese slakke wat verteenwoordigend is van aanlegsmeltings en 'n anleglegering is in alumina-kruisies by temperature van 1400°C, 1450°C, 1500°C en 1600°C met reagens behandel. Slakke bestaande uit 'n Suid-Afrikaanse mangaanerts met verskillende hoeveelhede kalk en verskeie sintetiese legerings met 'n verskillende silikoninhoud en mangaan-/ysterverhouding is in dergelike eksperimente gebruik. Hierdie eksperimente is uitgevoer in 'n vertikale weerstandsoond met volle temperatuurbeheer. Die verhouding tussen die slak en legering is ook gedurende die toets gewissel.

Die reliktietempo van MnO en die MnO uit die slag deur die silikon in die legering was uitsers vinnig en die grootste deel van die reaksie is binne vyf minute voltooi. Die sterk eksotermiese aard van die reaksie het 'n aansienlike ontwikkeling van hitte by die slag-legeringtussenlik toegeneem gehad wat konvensionele roering van die inhoud van die kroesie veroorsaak het en die reliktietaempo verhoog het.

Ewegig is gewoonlik na vyftien minute bereik. Die belangrike beperking op die herwinning van mangaan is die vereiste dat die silikoninhoud van die legering aan 'n maksimum spesifikasie van 2 persent moet voldoen. Hoër silikonkonsentrasies van tussen 8 en 12 persent in die finale legering bevorde goeie manganseherwinninge uit die slag, maar aangesien so 'n legering nie verkoop kan word, moet laer herwinninge blykbaar gevaar groot word. In legerings met 2 persent silikon is die lae aktiwiteit van die silikon verantwoordelik vir die swak herwinning van mangaan.

Die aktiwiteit van MnO in die slag kan verhoog word deur matige byvoegings van CaO en klein hoeveelhede MgO d.w.s. deur die basieseiteit van die slag te verhoog.

Introduction
In 1974, Mikolajczak predicted an increased demand for refined ferromanganese alloys due to increased use of the Linz–Donawitz (L.D.) process, as well as increased production of thinner finished steel products necessitating the use of manganese alloys with low-carbon contents. At that time, South Africa was rated as the sixth largest producer of medium-carbon ferromanganese by the Perrin process. At the beginning of 1974, the two 1,2 MV.A furnaces that had been used to produce low-carbon ferromanganese in South Africa were closed down because the operation was not economically feasible. At that time it was realized that there was a lack of fundamental knowledge in this field, and the Pyrometallurgy Research Group of the National Institute for Metallurgy (NIM) was asked by the Technical Subcommittee of the South African Ferro Alloy Producers’ Association to undertake an investigation into the relations between slags and alloys associated with the production of low-carbon ferromanganese.

The objects of this research were to determine the rate of reaction between the slags and alloys associated with low-carbon ferromanganese, and to measure the state of equilibrium attained. A further important problem requiring investigation was the oxidation of the slag, and to some extent of the metal. A range of synthetic manganese oxide slags and slags based on manganese ore were used in conjunction with several synthetic ferromanganese alloys and a typical alloy from a ferromanganese plant. The ferro-alloy industry was particularly interested in the recovery of manganese and the utilization of silicon.

As the slag and the alloy phases are complex, a mass-transfer model was devised for the reaction between the slag and the alloy relating to the transfer of manganese from the slag to the alloy and the transfer of silicon from the alloy to the slag. This model permits the final chemical composition of both the slag and the alloy to be determined if the initial compositions of both phases and the change in mass of the alloy as a result of the mass transfer during reaction are known. The model was extended to cover the various stages of reaction between the phases and to include the simultaneous reduction or oxidation of the slag phase by a gaseous phase. The initial oxidation state of the manganese before any reaction occurred between the slag and the metal was...
studied in the preliminary investigation of the slag-forming components.

Choice and Preparation of Materials

The compositions of most of the slags were chosen to represent industrial slags associated with the production of medium-carbon ferromanganese by the Perrin process as well as the single-stage low-carbon ferromanganese process that has been abandoned in South Africa. In this process, manganese ore, burnt limestone, and ferromanganese silicide are reacted simultaneously in a small electric-arc tilting furnace by a batch process.

A typical South African manganese ore, i.e., Mamatwan ore, was used in the preparation of several slags. Ferromanganese silicide from an actual plant was used for many of the reactions, but several synthetic alloys were used in this investigation to demonstrate the effect of variations in the silicon content and of the manganese-to-iron ratio on the recovery of manganese.

The non-stoichiometric behaviour of MnO was studied by Davies and Richardson but, for the conditions related to this field of investigation, there was some uncertainty about the oxidation state of the manganese in the slag phase. In the present investigation, preliminary tests were carried out on the deoxidation behaviour of MnO, since this oxide was selected as the source of manganese oxides for the slag phase. MnO was chosen because the exact quantity of manganese in the slag could be determined easily by calculation of the amount of manganese in the MnO, which is the source of manganese oxides for the slag phase. MnO was chosen because the exact quantity of manganese in the slag could be determined easily by calculation of the amount of manganese in the MnO. Furthermore, the amount of oxygen removed (or deoxidation) during the making of a slag premelt could be determined and, hence, the oxidation state of the manganese could be calculated. The synthetic slags were prepared by the weighing of pure chemical compounds to make up a total mass of 25,000 g. These slags can be divided into four groups, as follows:

1. lime-ore melts (approximately 50 per cent MnO),
2. high-grade slags (approximately 30 per cent MnO),
3. low-grade slags (15 to 20 per cent MnO), and
4. discard slags (less than 15 per cent MnO), which are slag products.

Lime-ore melts are associated with the Perrin process, high- and low-grade slags are produced in electric-smelting furnaces for the production of high-carbon ferromanganese, and discard slags are produced by furnaces for the production of ferromanganese silicide in which the MnO content can be as low as 5 per cent. The low-grade slag can be regarded as being representative of the final slag composition from the process for the production of low- to medium-carbon ferromanganese. The complete analyses for the range of slags used in the experiments and those for the Mamatwan ore are shown in Table I, only those for the discard and low-grade slags being omitted. The predried pure chemical components comprising the three slags were weighed in the proportions shown in Table I and then mixed thoroughly in a pestle and mortar. The ore-based slags were prepared by weighing of the components on a chemical balance and mixing in a pestle and mortar. The Mamatwan ore was crushed to material smaller than 100 mesh (Tyler). The only component added to these ore-based slags was pure CaO in the following proportions: 10, 20, 30, and 40 per cent by mass. An ore melt consisting solely of Mamatwan ore was also prepared to demonstrate the reaction of an unfluxed ore with ferromanganese silicide.

All the premixed slag-forming components were stored in a desiccator until required for premelting. The slag-forming powders were added to an alumina crucible and were weighed on a chemical balance. To form the pre-molten slag, the crucibles and their contents were subsequently heated to 1500°C in a small chamber furnace.

Prior to the fusion process, all the volatile constituents (i.e., carbon dioxide and water) were removed from the ore and the MnO, and other higher oxides of manganese in the ore were thermally deoxidized. It has been shown that Mamatwan ore consists essentially of braunite, hausmannite, and some calcite.

TABLE I

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Mammatwan ore</th>
<th>Calcinated at 1200°C* (mass loss from ore=17.4)</th>
<th>Lime-ore melt (standard slag)</th>
<th>High-grade slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>32.7</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>25.0</td>
<td>66.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Mn3O4</td>
<td>2.8</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>4.0</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>12.1</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>2.3</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.2</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>SiO2</td>
<td>4.8</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>39.4</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>4.2</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>CaO/MgO</td>
<td>5.2</td>
<td>61.2 (55)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>CaO+MgO ratio</td>
<td>3.0</td>
<td>8.0 (8.0)</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

*Mass loss from ore=17.4.

†The CaO/MgO ratio in the synthetic slags representing the lime-ore melt was varied from 2:1, 3:1, 5:1, and 1:1, and in the high-grade slag from 10:1, 9:1, 8:1, 1:1, and 0.5:1. 1

‡The (CaO+MgO)/SiO2 ratio in the synthetic slags representing the lime-ore melt was not varied, but in the high-grade slag the following ratios were used: 6:1, 5.67:1, 5:1, 1.8:1, 1.53:1, 0.75:1, and 0.4:1.
The industrial ferromanganese silicide was crushed to material smaller than 100 mesh; its chemical composition (in per cent by mass) was as follows: manganese 65.2, silicon 22.5, iron 11.1, and carbon 0.47. The synthetic alloys were made from pure metallic powders that were weighed on a chemical balance in the proportions shown in Table II. The total mass of the metal was 12,500 g. The metal powders to comprise the alloys were premelted in alumina crucibles in a vertical molybdenum-wound resistance furnace at a temperature of 1500°C in a reducing atmosphere of hydrogen and nitrogen in a ratio of 0.33. The alloy was then crushed to material smaller than 100 mesh before being reacted with the slag.

Experimental Techniques

The thermal behaviour of the manganese oxides during the premelting of the slag phase was studied with the aid of a Stanton thermal microbalance. The balance has full atmosphere control and was operated at a controlled heating cycle from room temperature to 1500°C at the rate of 6.7°C per minute. Hahn and Muan[5], who studied phase equilibria in the system Mn2O3-MnO-MnO2, mention that the various oxides of manganese are stable crystalline phases that can be converted from one oxidation state to another by variation of the temperature and of the partial pressure of oxygen. The present investigation of the high-grade and standard slags and Mamatwan ore was aimed at a determination of the degree of deoxidation of the higher oxides of manganese. Samples of 5,000 g were used for these tests, the samples being placed in small, fine-grained, low-porosity recrystallized-alumina crucibles and heated in a thermal balance. The crucibles were cylindrical, being 40 mm in height and 30 mm in inside diameter.

The tests involving the reaction between the slags and the alloys were carried out in a vertical molybdenum-wound resistance furnace. The chosen mass of alloy was placed on top of the premolten slag in the alumina crucible, which had been reweighed after the premelting stage. The total mass of the crucible, the slag, and the alloy was recorded, and the crucible was placed in a graphite holder. The holder was then raised slowly into the furnace, which was flushed continually with spectrographic pure argon. After the crucible and its contents had reached a temperature between 1200°C and 1250°C (i.e., below the liquidus temperatures of both the slag and the alloy) while being held in the furnace tube immediately below the hot zone, the crucible was rapidly introduced into the hot zone. The preset temperature of this zone was 1500°C for most of the tests, although temperatures of 1400°C, 1450°C, and 1600°C were also used.

The furnace temperature was controlled by a Eurotherm phase-angle thyristor unit on which adjustments can be made for temperature overshoot, temperature undershoot, and current limit, as well as temperature control by way of a Pt–6% Rh/Pt–30% Rh thermocouple positioned above the sample in the centre of the reaction tube in the central region of the hot zone. A second thermocouple of the same type, which was used to monitor the temperature of the sample from beneath the crucible, was introduced by way of the support rod for the graphite-crucible holder. The apparatus is illustrated in Fig. 1.

It was assumed that the reaction between the slag and the alloy had commenced when the surface of the molten alloy had disappeared beneath the slag. Very little reaction took place during this incubation period preceding the sinking of the alloy through the slag layer. The reaction was studied through the observation port at the top of the furnace work tube, and it was seen that considerable stirring of the contents of the crucible took place due to the strongly exothermic nature of the reaction.

During the raising of the sample holder and the crucible plus contents into the hot zone of the furnace, a drop in temperature of approximately 25°C occurred within the hot zone. However, the preset temperature was rapidly restored because of the relatively large heat capacity of the furnace and the quick response of the thyristor unit, which increased the power input to the furnace to meet the sudden demand created by the shock introduction of the sample holder and crucible plus contents. Some overheating of the sample environment also took place during the exothermic stage of the reaction, although temperatures much higher than 20°C above the preset value seldom occurred. However, this overheating within the slag and the alloy phases appeared to generate temperatures far above the 20°C measured externally from the crucible, and this sharp increase in temperature had a marked influence on the
rate of the reaction and hence on the approach to equilibrium between the slag and the alloy phases.

Studies on the rate of reaction were hampered by the uncontrollable nature of the reaction between the slag and the alloy, but samples were nevertheless withdrawn from the furnace at selected times from the start of the reaction and quenched in air. The sample within the crucible was protected from oxidation during this period by a special refractory lid. After the crucible had cooled, it was removed from the graphite holder and the contents of the crucible were broken out for weighing of the alloy bead. From the change in mass of this alloy bead, the transfer of silicon and manganese could be calculated by use of the mathematical expression derived from the mass-transfer model proposed by Baraza. Confirmation of the predicted analyses of the resulting slag and alloy was obtained by chemical analysis of a cross-section of samples of the slag and the alloy. These experiments were extended to include reactions in oxidizing and reducing environments. The argon used to flush the work tube was replaced with air or, alternatively, with hydrogen and nitrogen in a ratio of 3 to 1. During these experiments, the change in the total mass of the crucible was noted so that the degree of oxidation or reduction of the manganese oxides could be determined.

**Dissociation of MnO₂ and Ore**

The thermogravimetric tests carried out in air or argon on the slag representing the lime-ore melt and the high-and low-grade slags established that MnO₂ deoxidizes to Mn₃O₄, which is a 1-to-1 ratio of the Mn₃O₄ and MnO oxide states (i.e., half Mn⁴⁺ and half Mn²⁺) irrespective of the type of slag being melted. The dissociation of this stable oxide form was completed by the time the temperature of the furnace linked to the Stanton thermal balance had reached 1200°C. The application of the mass-transfer model to the system under consideration became feasible once the resulting oxidation state in the premelted slag had been determined.

The premelting in the chamber furnace in air of the many slags used in the study of reactions between the slag and the alloy confirmed that the oxidation state resulting from dissociation was Mn₃O₄. The mass of oxygen lost from a given mass of MnO₂ was used as the determining factor.

**Reaction between Slag and Alloy**

Various factors affect the rate of reaction and the equilibrium between the slag and the alloy.

**Temperature**

The results for the reactions conducted at the four selected temperatures (1400°C, 1450°C, 1500°C, and 1600°C), are shown in Fig. 2. The calculated values for the mass of manganese transferred from the standard slag to the plant alloy, based on the mass-transfer relation shown in equation (1), agreed closely with the results based on analysis of the alloy after reaction. Table III gives a comparison of the results for various reaction times at 1500°C. The changes in composition...
for manganese and silicon in the slag and the alloy are shown in Fig. 3. The equation used for calculation of the mass transfer of manganese was

$$\Delta M_{\text{Mn}} = 1.343 \Delta M_{\text{OBS}} + 0.343M_{\text{Mn}}(1 - X), \quad (1)$$

where $\Delta M_{\text{Mn}}$ is the mass of manganese transferred from the slag to the alloy,

$\Delta M_{\text{OBS}}$ is the net change in the mass of the alloy,

$M_{\text{Mn}}$ is the number of grams of manganese initially in the slag, and

$X$ is the fraction of oxygen lost from a given mass of $\text{MnO}_2$ in the primary slag during preheating.

The derivation of this equation is shown in the Addendum.

Fig. 4 shows the variation in the distribution ratio $(\text{MnO})/\text{Mn}$ with changes in temperature from 1400°C to 1600°C, the minimum value occurring at 1500°C.

**Ratio of Slag to Alloy**

Fig. 5 shows the variation in the recovery of manganese

**TABLE III**

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>Temperature</th>
<th>Analytical results</th>
<th>Theoretical results based on derived mass transfer equation (1)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>°C</td>
<td>Plant alloy</td>
<td>Standard slag</td>
</tr>
<tr>
<td>5</td>
<td>1500</td>
<td>0.854</td>
<td>0.047</td>
</tr>
<tr>
<td>10</td>
<td>1500</td>
<td>0.878</td>
<td>0.031</td>
</tr>
<tr>
<td>15</td>
<td>1500</td>
<td>0.864</td>
<td>0.037</td>
</tr>
<tr>
<td>20</td>
<td>1500</td>
<td>0.858</td>
<td>0.048</td>
</tr>
<tr>
<td>25</td>
<td>1500</td>
<td>0.862</td>
<td>0.037</td>
</tr>
<tr>
<td>30</td>
<td>1500</td>
<td>0.861</td>
<td>0.032</td>
</tr>
<tr>
<td>35</td>
<td>1500</td>
<td>0.851</td>
<td>0.047</td>
</tr>
<tr>
<td>5</td>
<td>1600</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Underlining denotes that the constituent is in the metal phase, and parentheses that the constituent is in the slag phase.

* The composition of the Mn and Si and $(\text{MnO})$ and $(\text{SiO}_2)$ in the products was calculated from the initial composition of the alloy and slag and from the Mn and Si mass transfer, which in turn was determined by weighing the alloy bead after reaction for the given time and substituting the value in the mass-transfer equation (1).

Fig. 4—The effect of temperature on the manganese distribution ratio at equilibrium

Fig. 5—The effect of the slag-to-alloy ratio on the recovery of manganese and on the distribution ratios of manganese and silicon at equilibrium
Fig. 6 - The effect of the amount of CaO or SiO₂ added and the final CaO/SiO₂ basicity ratio on manganese recovery and distribution ratio.

Fig. 7 - The effect of the initial basicity ratio on the recovery of manganese from high-grade slag.

Fig. 8 - The relation between the final basicity ratio and the manganese distribution ratio at equilibrium.

Fig. 9 - The effect of the chosen CaO/MgO ratio on the manganese recovery and distribution ratio at equilibrium.
and the distribution ratio (MnO)/Mn with change in the slag-to-alloy ratio from 5 to 0.83, the minimum value occurring at a ratio of 1.

**Composition of Slag and Alloy**

The variation in manganese recovery and distribution ratio (MnO)/Mn with additions of CaO, MgO, and SiO₂ and with changes in the final CaO/SiO₂ ratio, the initial and final (CaO+MgO)/SiO₂ ratio, and the CaO/MgO ratio are shown in Figs. 6, 7, 8, and 9 respectively.

The variation in manganese recovery and distribution ratio with increasing initial silicon in the alloy is shown in Fig. 10. Initial silicon contents (per cent by mass) of 10, 22.5, 30, 50, 70, and 100 were used. The minimum distribution ratios for (MnO)/Mn were obtained for the following instances:

- an initial basicity ratio (CaO+MgO)/SiO₂ of 1.33,
- a basic oxide ratio of CaO/MgO of slightly more than 3,
- and an initial silicon content of 30 per cent.

No minimum value for (MnO)/Mn was obtained for increases in the CaO/SiO₂ ratio, since dilution of the (MnO) results in a levelling off in the recovery of manganese up to a ratio of 3. The optimum amount of CaO added for maximum recovery of manganese was 20 per cent by mass, as shown in Fig. 6.

**Discussion**

**Phase Systems**

According to Muan, MnO₂ is stable only up to 425°C, dissociating to Mn₂O₃ and then to Mn₃O₄ with increasing temperature. The Mn₃O₄ oxidation state was found to be very stable under neutral or oxidizing conditions up to temperatures of 1600°C, and lower oxidation states in the form of increasing ratios of Mn²⁺ to Mn³⁺ were achieved only in reducing atmospheres of either carbon monoxide or hydrogen. The monitoring of the change in mass of a given initial quantity of MnO₂ provided a convenient reference for determination of the resulting oxidation state. The mechanism of dissociation of MnO₂ was not studied since the only aim of these tests was to establish the resulting oxidation state of manganese after premelting of the initial slags prior to testing of the reaction between the slag and the alloy. The slag-forming components had no noticeable effect on the degree of dissociation of the MnO₂ since Mn₃O₄ was formed in all the unreduced premelted slags. The melting characteristics and liquidus temperatures of manganese oxide slag systems have been studied extensively. The following systems have been investigated:

- the MnO-SiO₂ system by Glasser, the MgO-MnO-SiO₂ system by Glasser and Osborn, the CaO-MnO system by Ribound and Muan, and the MgO-CaO-MnO-Al₂O₃ system by Warren. In this project, the liquidus temperatures for most of the slags considered were expected to be below 1500°C in accordance with those findings, and this prediction was confirmed during the premelting tests. The only slags with higher liquidus temperatures were those with MgO/CaO ratios greater than 0.66 for a basicity ratio (CaO+MgO)/SiO₂ of 1.33.

**Rate of Reaction**

Very rapid reaction between the slag and the alloy was observed at temperatures of 1400°C, 1450°C, 1500°C, and 1600°C, and equilibrium was usually reached within 5 to 10 minutes from the start of reaction. Two reactions were observed, the first taking place mainly during the incubation period before final melting of the alloy head through the slag. Table IV shows the decrease in value with time for the analyses of the MnO₃ or Mn⁺⁺ concentration during this stage as given by the following de-oxidation reaction:

\[ 2(MnO_3) + Si = 4(MnO) + (SiO_2), \]

i.e., \( 4(Mn^{2+}) + Si = 4(Mn^{3+}) + (Si^{4+}) \).

**TABLE IV**

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Analytical value % by mass</th>
<th>Theoretical value % by mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MnO₂</td>
<td>Mn₃O₄</td>
</tr>
<tr>
<td>Premelt (std slag)</td>
<td>51.51</td>
<td>18.11</td>
</tr>
<tr>
<td>0.1</td>
<td>49.58</td>
<td>6.38</td>
</tr>
<tr>
<td>0.5</td>
<td>38.58</td>
<td>3.25</td>
</tr>
<tr>
<td>1</td>
<td>32.41</td>
<td>0.27</td>
</tr>
</tbody>
</table>

*Values of 0.0 are assumed since all the Mn⁺⁺ is reduced to Mn⁺⁺ prior to the commencement of reduction of Mn⁺⁺ to metal.
The Mn\(^{2+}\) and Mn\(_3\)O\(_4\) concentrations are also shown in Table IV.

The second reaction took place between the MnO or Mn\(^{2+}\) and the remaining silicon in the alloy and is shown by the reaction for the recovery of manganese:

\[ 2(MnO) + Si = 2Mn + (SiO\(_2\)) \]

i.e., \[ 2(Mn^{2+}) + Si = 2Mn + (Si^{4+}) \] (3)

The influence of the chosen system temperature on the reaction was masked by the exothermic heat liberated from the reaction at the interface between the slag and the alloy. The effect of temperature on the rate of reaction between the slag and the alloy could therefore not be studied satisfactorily. After the rapid part of the reaction had been completed during the initial 5 minutes, a much slower rate of reaction was observed during the final 10 minutes before the attainment of equilibrium. Stirring of the alloy and the slag failed to increase the rate of reaction and merely increased the Al\(_2\)O\(_3\) content of the slag.

The results of these tests indicate that the conventional stirring caused by thermal gradients between the reaction interface and the bulk phases was sufficient to assist in the transport of the reactants and products to and from the slag-alloy interface. The diffusion of the individual species could therefore not be regarded as being responsible for the rate-controlling stage of the reaction as it was for the system studied by Daines and Pehlke\(^{15}\). That system contained very low concentrations of Mn\(_2\)O\(_3\) and silicon, and the evolution of heat was negligible.

The fact that no marked changes can be detected in reaction rates with temperature or stirring complicates the modelling of this system, and conventional techniques for solving the rate of reaction cannot be readily applied. The chemical reaction at the interface between the slag and the alloy is apparently the rate-determining stage, even though the influence of furnace temperature could not be detected with the chosen experimental approach. The rate of heat generated from the slag-alloy interface by means of differential thermal analysis could possibly provide some reliable data for the reaction rate versus temperature under the non-isothermal conditions prevailing. On this laboratory scale, the reaction rate was rapid and the dimensions of the reaction vessel small; therefore, it was not considered to be a fully representative system that could be used for an adequate study of plant conditions, and the subject was not pursued any further. Larger-scale plant operations could be regarded differently, and the reaction rates for various types of mixing are being investigated further.

Factors Affecting Equilibrium

The state of equilibrium attained between the slag and the alloy was judged to have been reached once the net transfer of manganese from the slag to the alloy and of silicon from the alloy to the slag had ceased. The influence of temperature, the ratio of the slag to the alloy, and the compositions of the slag and the alloy on the equilibrium conditions were examined by plotting of the manganese distribution ratio against the chosen variable. Distribution ratios for silicon, i.e., \((SiO\(_2\))\)/Si, were also plotted in some instances.

The values for the concentrations of manganese and silicon in the alloy and their respective oxides in the slag were expressed as mass fractions rather than as activity values since, in most instances, such values were not available in the literature. The distribution ratios for (MnO)/Mn and (SiO\(_2\))/Si were derived from these values from the mass fractions. The apparent equilibrium constant was expressed as

\[ K_{\text{Mn, Si}} = \frac{(MnO) \cdot Si}{Mn} \]

which is the same expression as that used by Heynert et al.\(^{17}\), and was determined by use of mass fractions.

Temperature

The results for the determination of the influence of temperature on the distribution ratio of (MnO)/Mn suggest that a minimum value occurs at 1500°C. The higher values for the (MnO)/Mn ratio at 1400°C and 1450°C possibly occurred because these temperatures are close to the liquidus temperature of the slag and the reaction might have been incomplete or subjected to a somewhat different reaction mechanism. The higher distribution values at 1600°C can possibly be explained by the less-favourable thermodynamic relations, i.e., the \(\Delta G\) value is less negative at 1600°C than at 1500°C. The overheating of the two phases as a result of the exothermic reaction could possibly also be responsible for this minimum point, as shown in Fig. 4. The higher (MnO)/Mn distribution ratio at 1600°C could have been the result of a small vapour loss of MnO from the slag, causing less manganese to be reduced to the metal. A small overall loss in mass from the crucible was observed during these high-temperature tests that would partly explain the higher (MnO)/Mn distribution value at 1600°C.

Slag-to-alloy ratio

From the results of the experiments in which the mass of the alloy was increased in relation to the constant initial mass of the slag (25 g), four stages of change in mass can be observed. For small additions of alloy (less than 3.28 g), there was a net mass loss from the alloy. Insufficient silicon was available from the small quantity of alloy to reduce all the Mn\(^{2+}\) to Mn\(^{2+}\). Hence, either no reduction of manganese occurred or, alternatively, even if some manganese was formed, insufficient manganese was gained to cause a net mass gain because of the relatively greater mass loss of silicon. The first stage covers the region from zero mass loss up to the stage where no further increase in mass loss with increase in alloy mass occurs, i.e., the minimum mass point. The second stage lies between this minimum point and the so-called break-even point, where the alloy mass has returned to its original value. In this stage, the mass gain due to transfer of manganese is sufficiently great to more than compensate for the mass loss of silicon, and this results in a net gain up to the break-even point. The third stage of mass change occurred when further additions of alloy were made and an overall net increase in mass took place. The fourth stage of mass change is characterized by a negligible increase in manganese recovery for increasing addition of the alloy.

The activity of the MnO in the slag therefore appears
to be the limiting factor, which, in this instance, results in no further recovery of manganese. The optimum ratio of the slag to the alloy for the standard slag and plant alloy appears to be close to 1, as shown in Fig. 5, where the minimum (MnO)/Mn value was 0.170. The (SiO₂)/Si value of 3.16 is not favourable at this stage since the alloy contains far too much silicon to meet the required silicon specification for a low-carbon ferromanganese, i.e., less than 2 per cent. The silicon content was, in fact, still 10.82 for this particular slag-to-alloy ratio. The optimum (SiO₂)/Si ratio was achieved for a slag-to-alloy ratio of 2.5.

Composition of alloy and slag

Increase of the silicon content of the alloy up to a value of 30 per cent decreased the (MnO)/Mn distribution ratio, as can be seen in Fig. 10. The minimum distribution ratio was 0.169. When the silicon content of the initial alloy was increased to more than 30 per cent, a decrease in the manganese distribution ratio occurred. Very little reaction took place when pure silicon was reacted with the slag. The only possible reason that can be postulated is that surface tension at the interface inhibits diffusion across the reaction interface. Even when the contact area at the interface was increased by stirring, virtually no reaction occurred. The silicon alloy formed a spherical bead, unlike the flat beads formed from alloys containing smaller quantities of silicon, which suggests that greater surface-tension effects are present in the alloy having a high silicon content.

The slag composition had considerable influence on the final state of equilibrium attained. When CaO, MgO, and SiO₂ were added singly or in combination, marked changes occurred in the recovery of manganese and in the distribution ratios between the slag and the alloy. SiO₂ is one of the reaction products; therefore, as the reaction proceeds, the basicity ratio expressed as (CaO+MgO)/SiO₂ decreases. The addition of SiO₂ to MnO₂ to form a premelted slag that was reacted with the alloy in a ratio of 2 resulted in a dramatic decrease in the manganese recovered from the slag, as shown in Fig. 6.

When the basicity ratio of the standard slag (expressed as CaO/SiO₂) is increased, there is a marked decrease in the (MnO)/Mn distribution ratio, with a corresponding increase in the recovery of manganese and in the MnO/Mn ratio (see Fig. 7). The optimum MnO/Mn ratio for the slag was observed for an initial ratio of 1.33 in the high-grade slag (see Fig. 7). The (SiO₂)/Si value of 3.16 is not favourable at this stage since the alloy contains far too much silicon to meet the required silicon specification for a low-carbon ferromanganese, i.e., less than 2 per cent. The silicon content was, in fact, still 10.82 for this particular slag-to-alloy ratio. The optimum (SiO₂)/Si ratio was achieved for a slag-to-alloy ratio of 2.5.

Theory of Slag-Alloy Equilibrium

The activity of the MnO in the slag and of the silicon in the alloy are of major interest in attempts to understand the state of equilibrium attained.

Activities in the slag phase

Very few fundamental thermodynamic data are available for the slag compositions associated with the production of low- to medium-carbon ferromanganese. The trends observed by Warren¹⁴ for similar slags associated with the production of high-carbon ferromanganese could be applicable to the behaviour of the slags studied in this project. The addition of limited amounts of CaO to the slag increases the activity coefficient of MnO and reduces the viscosity of the slag. Larger additions of CaO cause an increase in the liquidus temperature and overall dilution of the MnO. Partial replacement of the additions of MgO by the addition of MgO can result in a corresponding improvement in the manganese distribution ratios as shown in Fig. 9. MgO has a lower molecular mass than has CaO, and there is an overall increase in the mole fraction of the basic fluxes. However, MgO tends to increase the liquidus temperature of the slag at far lower concentrations than does CaO, and hence the CaO/MgO ratio should not be less than about 3 for a slag with (CaO+MgO)/SiO₂ of 1.33 if optimum recoveries are to be obtained (see Fig. 9).

When the concentration of the basic oxides of Ca³⁺, Mg²⁺, and Mn²⁺ are low, these cations become associated with the larger ionic groups of SiO₂ and, as a result, very few O²⁻ anions exist. MnO therefore has a very low activity coefficient. As the content of the basic oxides is increased, the SiO₂ network is broken down into smaller anionic groups and more free O²⁻ ions are present. The role of these two basic oxides in breaking up the silicate network is even more important when secondary SiO₂ is formed as a product of the reaction. Warren¹⁴, Channon and See¹⁶, and Woollacott et al.¹⁷ discuss the physico-chemical properties of MnO slags in detail.

Activities in the alloy phase

Very little can be done to improve the activity of silicon in the alloy. Channon and See¹⁶ showed that ferro-silicon is a better silicon-containing alloy than is ferromanganese silicide because it has higher silicon activity. However, the manganese content of the resulting alloy is too low since 80 per cent is the minimum value specified. If silicon is added to iron, the activity of the silicon is far lower than would be the case for ideal liquids, and a similar deviation was found in the Mn–Fe–Si alloys used by Turkdogan and Hancock¹⁸, ¹⁹. The activity of silicon in the system Fe–Mn–Si–C is also low according to Tolstoguzov²⁰. The concentration of silicon drops as equilibrium is approached; therefore, extremely low silicon activities can be expected. High ratios of alloy to slag, or initial silicon contents in the alloy of up to 30 per cent, favour low (MnO)/Mn distribution ratios because of the relatively high silicon content of the alloy at equilibrium.

Equilibrium constants

If activity values are available for the MnO and SiO₂ in the slag and for the manganese and silicon in the alloy, the equilibrium constant is expressed as

$$K_{SI,Mn} = \frac{a_{Mn} a_{SiO_2}}{a_{MnO} a_{Si}}$$  \hspace{1cm} (5)$$

where $a$ is the activity of the component indicated by the subscript.

The compositions of the slag and alloy shown in Table V were similar to those of the slags investigated by
Warren\textsuperscript{14} and Sharma and Richardson\textsuperscript{21}, and those of the alloys studied by Ohtani\textsuperscript{22} and Rawling and Elliot\textsuperscript{23}. The approximate activity values were used in the calculation of the equilibrium constant. The compositions of the slag and the alloy shown in Table V resulted from the reaction between the standard slag and a synthetic alloy having an initial silicon content of 30 per cent. The slag-to-alloy ratio was 2, and the furnace temperature was 1500°C.

\[
K_{Si,Mn} = \frac{(0.85)^2 (0.10)}{(0.14)^2 (0.05)} = 73.7. \quad \quad (6)
\]

The value in equation (6) is in close agreement with McGannon's value\textsuperscript{24} of 76.2, which was obtained at 1600°C. Many of the apparent equilibrium values differ from this value as a result of the deviation of the SiO\textsubscript{2} and silicon activities from the ideal (see Table VI).

The other expression for the apparent equilibrium constant was \(K_{Mn,Si}\), and the values shown in Table VI range from 0.035 to 0.104. These values correspond fairly closely to those given by Heynert\textsuperscript{7} and Chan and See\textsuperscript{16} for similar basicity ratios in the final slag. As the alloy in equilibrium with the slag investigated by Heynert et al.\textsuperscript{7} was high-carbon ferromanganese, some difference in the distribution between the slag and the alloy can be expected.

**Conclusions**

1. At a temperature of 1200°C, MnO\textsubscript{2}, the initial oxide form of manganese used in these tests, dissociates thermally to Mn\textsubscript{3}O\textsubscript{4} in air. The higher oxides in the Mamatwan manganese ore were also expected to dissociate to Mn\textsubscript{3}O\textsubscript{4}. The composition of the slag did not alter the degree of deoxidation of MnO\textsubscript{2} to Mn\textsubscript{3}O\textsubscript{4}.

2. Investigation of the rate of reaction between the slag and the alloy is complicated by the fact that constant temperature cannot be maintained because of the strongly exothermic nature of the reaction. The rate of reaction is extremely rapid as a result of the geometry of the apparatus used for these tests, and stirring and furnace temperature in the range 1400°C to 1600°C had little effect on the rate. The mechanism that appears to result in rapid reaction is thermal convectional stirring.

3. The activity of MnO in the slag can be increased by additions of CaO until dilution of the MnO causes a decrease in the recovery of manganese. The optimum addition was 20 per cent by mass for pure

**TABLE V**

**ACTIVITY VALUES FOR COMPONENTS IN THE SLAG AND THE ALLOY AT EQUILIBRIUM**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Content, %</th>
<th>Approx. activity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>14.3</td>
<td>0.14</td>
<td>13</td>
</tr>
<tr>
<td>CaO</td>
<td>32</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>MgO</td>
<td>4.0</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>35.0</td>
<td>0.10</td>
<td>21</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>Approx. 5.0</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>Alloy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>84.5</td>
<td>0.85</td>
<td>22</td>
</tr>
<tr>
<td>Fe</td>
<td>7.5</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>Si</td>
<td>8.0</td>
<td></td>
<td>23</td>
</tr>
</tbody>
</table>

\[
\frac{\text{MnO}}{\text{MnO}_2} = \frac{73.7}{(0.85)^2 (0.10)} = 2.4.
\]

**TABLE VI**

**ACTIVITY VALUES FOR COMPONENTS IN THE SLAG AND THE ALLOY AT EQUILIBRIUM**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Activity value</th>
<th>K\textsubscript{Mn,Si}</th>
<th>K\textsubscript{Si,Mn}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>7.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>8.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
MnO₂ and about 30 per cent by mass for the Mamatwan ore. The addition of MgO instead of CaO according to mass percentage results in a moderate increase in the recovery of manganese down to a CaO/MgO ratio of 3 and a subsequent decrease in the recovery. The liquidus temperature of the slag melt was increased considerably by CaO additions of over 40 per cent or by ratios of CaO/MgO less than 3. The higher liquidus temperatures resulted in greatly impaired reaction conditions.

(4) The recovery of manganese increased considerably with decreases in the ratio of the slag to the alloy, the optimum slag-to-alloy ratio for manganese recovery being 0.8. However, this low ratio had two adverse effects: the low manganese and the high silicon contents of the alloy after reaction. A ratio of 2 is necessary to meet the required silicon and manganese specifications, i.e. 80 per cent and less than 2 per cent respectively for the alloy. In practice, under these conditions, lower manganese recoveries must therefore be expected.

(5) As the silicon content of the alloy increased up to 30 per cent, the recovery of manganese became higher. A decrease was observed in the recovery of manganese for silicon values of 50, 70, and especially 100 per cent. This unexpected decrease may be due to a change in the interfacial tension between the slag and the alloy that manifested itself as a tendency for the alloy to become increasingly spherical as the silicon content increased. High contents of the residual silicon were obtained in alloys with silicon values of 50, 70, and especially 100 per cent, which is that of the plant alloy. A higher ratio of slag to alloy would be required for an alloy with a silicon content of 30 per cent if the alloy product were to meet the required specifications. However, ferromanganese silicides having silicon contents of 30 per cent are considerably more difficult to produce than those with contents of 10 to 23 per cent.

(6) In summary, the implications of these laboratory tests on synthetic and plant starting materials is that, although the rates of reaction are rapid, the equilibria are unfavourable for plant operation. This means that relatively high MnO contents in the slag must be accepted in the conventional single-step slag–alloy reaction if 2 per cent silicon in the alloy (which is the specification) is to be achieved. The MnO in the slag can be decreased to some extent by an increase in the CaO or MgO, or both, up to a maximum basicity ratio of 1.33 for the high-grade slag. However, the results indicate that the single-step process as commonly practised is not suitable, and the reaction equilibria and rate of reaction indicate that multiple-contact techniques would favour the reaction. This aspect is to be the subject of further study.

Acknowledgements

Grateful acknowledgement is made to the Ferro Alloy Producers' Association for the research fellowship and additional financial support they provided, and to Professor D. D. Howat, Dr P. R. Jochens, and Mr S. S. Solmer-Olsen for their assistance during the work.

This paper is presented by permission of the National Institute for Metallurgy.

References


Addendum

The following two chemical reactions are used as the basis for the derivation of the mass-transfer model:

Reduction of the higher oxide state
$$2(MnO) + Si = 2(Mn) + (SiO_2) \quad (1)$$

Reduction of the lower oxide state
$$2(MnO) + Si = 2Mn + (SiO_2) \quad (2)$$

The alloy undergoes a change in mass during the reaction as it gains Mn in exchange for the Si it loses. This is according to reaction (2). The alloy can also undergo a loss in mass when Si is lost but no Mn is gained, as shown by reaction (1).

If the mass of the alloy at any specific stage during the reaction between the two phases is $M_{obs}$ and the resultant change from its original mass is $\Delta M_{obs}$, the following equation can be used to describe this change:

$$\Delta M_{obs} = \Delta M_{slag}^A - M_{obs}^A \quad (3)$$

where $M_{obs}^A$ = the initial mass of alloy.

The following are the most important parameters that concern reaction and subsequent mass transfer:

$\Delta M_{Si}^A$ = the mass transfer of Si from the slag to the alloy

$\Delta M_{Si}^A$ (Mn$^{3+}$) = the mass transfer of Si from the alloy to the slag for the reaction (Mn$^{2+}$→Mn$^{3+}$)

$\Delta M_{Si}^A$ (Mn$^{2+}$) = the mass transfer of Si from the alloy to the slag for the reaction (Mn$^{2+}$→Mn$^{3+}$).

The actual nature of the two transfer species is such that the use of the observed change in mass as an experimentally measurable quantity is feasible. The reason for this fact is twofold. Firstly, there is a factor of almost 2 in the ratio of the atomic mass of Mn to that of Si (54.94 and 28.06). Secondly, an exchange of 1 mole for 2 takes place according to reaction (2).

The alloy undergoes a change in mass during the reaction and subsequent mass transfer:

$$\text{Si} + O_2 = \text{SiO}_2$$

28.06 32

The value of $\Delta M_{Si}^A$ (Mn$^{3+}$) = $O_2$ (Mn$^{3+}$). $\frac{28.06}{32} = 0.8769. O_2$ (Mn$^{3+}$), (8)

where $O_2$ (Mn$^{3+}$) is the oxygen associated with the Mn$^{3+}$.

According to reaction (2), the ratio of Mn mass transfer to that of Si transfer can be written as

$$\frac{\Delta M_{Si}^A}{\Delta M_{Mn}^A} = 3.915 \quad (9)$$

If equations (8) and (9) are substituted into equation (6), the following expression is obtained:

$$\Delta M_{obs}^A = \Delta M_{Mn}^A - 0.8769. O_2 (Mn^{3+}) + \Delta M_{Mn}^A$$

$$3.915$$

$$= \Delta M_{Mn}^A \left(1 - \frac{1}{3.915}\right) - 0.8769. O_2 (Mn^{3+})$$

When the equation is solved in terms of $\Delta M_{Mn}^A$, an equation for the mass transfer of Mn, based on the observed change of mass of the alloy and the initial Mn$^{2+}$ content of the slag phase, can be derived:

$$\Delta M_{Mn}^A = 1.343. \Delta M_{obs}^A + 1.1777. O_2 (Mn^{3+}) \quad (10)$$

Now $O_2 (Mn^{3+}) = \frac{16(1-X)}{64.94} \times M_{Mn}^S$

$$= 0.2913 (1-X). M_{Mn}^S \quad (11)$$

where $M_{Mn}^S$ = the quantity of Mn in the slag in grams $X$ = the fraction of $O_2$ lost from a given mass of Mn$O_2$.

Equation (11) can be substituted into equation (10) to give the following general equation for the mass transfer of Mn:

$$\Delta M_{Mn}^A = 1.343. \Delta M_{obs}^A + 0.3431. M_{Mn}^S (1-X) \quad (12)$$

where $\Delta M_{Mn}^A$ = mass transfer of Mn

$$M_{Mn}^S = \text{mass of Mn in the slag}$$

$X$ = the $O_2$ fraction dissociated from Mn$O_2$. 

The proportion of Si transfer from the alloy to Mn transfer to the alloy will depend entirely on the ratio of Mn$^{3+}$/Mn$^{2+}$ in the slag phase at the commencement of reaction. $\lambda_{Si}^M$ (Mn$^{3+}$) is the change in mass associated with the reduction of Mn$^{3+}$ to Mn$^{2+}$. This amount of Si is directly related to the initial Mn$^{3+}$ content of the slag.

Under most atmospheric conditions, both Mn$^{2+}$ and Mn$^{3+}$ are contained in the slag phase, and therefore the theoretical stoichiometric quantity of Si required for complete reaction will depend on both the amount of MnO in the slag phase and the ratio of Mn$^{3+}$/Mn$^{2+}$.

From reaction (1), it can be noted that the Si is effectively combining with $O_2$ in the following manner:

$$\text{Si} + O_2 = \text{SiO}_2$$

28.06 32

The value of $\Delta M_{Si}^A$ (Mn$^{3+}$) = $O_2$ (Mn$^{3+}$). $\frac{28.06}{32} = 0.8769. O_2$ (Mn$^{3+}$), (8)