Equilibria Between Refined Ferromanganese/Silicomanganese Alloys and Silicate Slags at 1500°C

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Abstract

Slag Metal equilibria experiments were conducted between refined ferromanganese/silicomanganese alloys and silicate slags at 1500°C. It was found that the Si partition ratio increased and Mn partition ratio decreased with increasing basicty ratio. Carbon content of the alloy phase varied in the range 1.0 to 5.5%. Sulphur partition ratio also increased with slag basicity.

Introduction

Refined ferromanganese is produced by oxygen blowing of high carbon ferromanganese or by silicothermic reduction of high grade MnO slags depending on carbon content required in the final alloy. The system in these processes consists of the slag, metal and gas phases in which the components are given as Fe, Mn, Si and C for the metal phase and MnO, CaO, MgO, SiO_2 and Al_2O_3 for the slag phase. In refining, the transfer of the elements Mn, Si, C and O between phases form the basic part of the process and are controlled by the equilibrium conditions in the system. To achieve a controlled refining and to be able to bring the phases to the required compositions, the equilibrium conditions and the controlling parameters have to be investigated in detail. The sound knowledge of the equilibrium conditions is necessary to define the operating parameters of the refining process. The parameters defining the equilibrium conditions would eventually control the refining process regarding the equilibrium concentrations of the elements of the slag and metal phases. The effects of the parameters such as the compositions of the slag and metal phases, in particular, the basicity ratio, CaO/MgO ratio, MnO and SiO_2 contents of the slag and the Mn, Si and C contents of the alloy on the equilibrium state need to be studied in detail. There are also strict requirements of the impurity elements such as sulphur and phosphorus in the metal phase.

There has been a number of investigations studying the equilibria between the MnO slags with ferromanganese or silicomanganese alloys at carbon saturation levels[1-13] Very few studies however have been done on the same systems at refined carbon levels which still require a further study on this subject [14-18]

Typical ferromanganese slags consist of MnO, CaO, SiO_2, MgO and Al_2O_3. The MnO activity was studied by Mehta and Richardson in various binary and ternary systems of the oxides present in the ferromanganese slags[1]. The activities of MnO and SiO_2 were also studied in the above system[2] and in the slag-metal sytem[11,12] previously. The distribution ratios of Mn and Si between metal and slag phase were determined by Turkdogan and Hancock at carbon saturated systems[3]. The reduction of MnO from the blast furnace slag and the distribution of Mn in the slag and alloy were studied by Benesch[8].

The purpose of this study can be summarized as follows:
1. Determination of manganese and silicon distributions between the alloy and slag phases formed after the equilibrium has been established between the refined ferromanganese/silicomanganese alloys and the MnO slags.
2. Determination of the carbon content of the alloy phase in equilibrium with the slag.
3. Study of the influence of the slag and alloy compositions on the distribution ratios of Si and Mn and on the content of C in the alloy with respect to the parameters such as the basicity ratio, CaO/MgO ratio, SiO_2 and MnO contents of the slag phase and the silicon and carbon contents of the alloy phase.
4. Determination of sulphur distribution between the metal and slag phases.

Experimental

Work is conducted for equilibrium in the system of Mn-Fe-Si-C-(S), MnO-CaO-MgO-SiO_2-Al_2O_3 and N_2+CO. The slag compositions are chosen according to the model applicable to the Bob-Jenkins statistical method within the ranges encountered in the industry (Table 1). The alloy compositions are chosen as typical of ferromanganese and silicomanganese alloys containing sulphur with four different carbon contents for the ferromanganese (Table 2). Gas atmosphere is a mixture of N_2 and CO at a volume ratio of approximately 50% each, supplying an oxygen partial pressure of 3.17×10^{-17} atm. in the gas phase. The purpose of using N_2 gas as a part of the gas atmosphere in the system is to prevent BN crucible which would otherwise decompose at low nitrogen partial pressures. A graphite crucible is also used enveloping the BN crucible to give it an additional physical support and protection. Graphite also maintains a fixed oxygen partial pressure in the presence of CO.

Duration of each equilibrium experiment is chosen as 24 hours which is found sufficient according to a previous work[12]. The equilibrated samples are separated into their slag and metal parts and each part is submitted to chemical analysis for its constituents to determine the equilibrium concentrations. Distribution ratios of Si(slag)/ Si(metal) and Mn(slag)/Mn(metal) are determined from

analytical results. The effects of the basicity ratio, CaO/MgO ratio, MnO and SiO_2 contents of the slag on the distribution ratios and on the C and S contents of the metal are discussed. Activities of Mn are calculated by using the experimental data, from known activities of MnO of the slag.

Apparatus

A vertical furnace with an alumina reaction tube was used in the experiments. The furnace was heated by Mo wire wound around another alumina tube encircling the reaction tube. Mo wire was protected by decomposed NH_3 . Furnace temperature was controlled by a digital controller (RKC REX-P-90) using a Pt-6%Rh/Pt-30%Rh type B thermocouple which was inserted through the furnace shell towards the winding tube. Temperature of the hot zone was measured with another B type thermocouple inserted through the reaction tube. The accuracy of temperature was within 5°C at 1500°C. The reaction tube was sealed with flanges at both ends permitting the passage of the reaction gasses only. A mixture of CO and N_2 , each forming about 50% of the total reaction atmosphere was purged through the reaction tube at the total rate of 200 ml per minute. The reaction gasses were passed through various gas cleaning agents and a deoxidation furnace containing Cu at 500°C before being flushed through the furnace. A manometer with a gas mixing system was used in order to supply a homogeneous gas mixture at required proportion. A two hole alumina rod with Mo wire passing through each hole was used to suspend the sample at the hot zone of the furnace which facilitated quenching of the samples by passing current through these wires and melting the part of the wire holding the crucible.

Preparation of the Samples

Slag Samples:
CaO, MgO, SiO_2 and Al_2O_3 are weighed in desired proportions, mixed homogeneously in an agate mortar under acetone and pressed into pellets which are later calcined at 1200°C for 12 hours and kept in a sample desiccator. Before each run, the pellets are ground in an agate mortar and mixed with required amount of MnO and placed in a boron nitride crucible with the alloy sample prepared accordingly as described below.

Alloy Samples:
Electrolytically pure Fe, Mn, Si, spectrographic C and pure FeS (to provide equivalent amount of S) are weighed in required proportions, mixed homogeneously and placed in a boron nitride crucible with the corresponding slag samples.

Procedure

The alloy mixture of 4 g was placed at the bottom of the BN crucible and slag pellet weighing 4 g was placed above the alloy in the same crucible. The BN crucible containing the alloy and slag was inserted into a slightly larger graphite crucible which was not in contact with the sample. Presence of graphite and CO gas in the system provided $3.17X10^{-17}$ atm partial pressure of oxygen in the reaction zone at 1500°C as will be shown later. The graphite crucible with BN crucible inside was suspended from the top of the work tube to the hot zone. Boron nitride was found stable under existing experimental conditions. The equilibration time was chosen as 24 hours as discussed previously. The equilibrated samples were quenched by dropping them into a water tank which was sealed and attached to the bottom of the work tube.

Table 1. Initial composition of the Slag samples

No	MnO	CaO	MgO	SiO_2	Al_2O_3	(CaO+MgO)/SiO_2	CaO/ MgO
1	5.0	20.0	10.0	60.0	5.0	0.50	2.00
2	5.0	35.0	10.0	45.0	5.0	1.00	3.50
3	25.0	20.0	10.0	39.0	5.0	0.75	2.00
4	25.0	35.0	10.0	24.0	5.0	1.80	3.50
5	5.0	27.5	5.0	56.5	5.0	0.57	5.50
6	5.0	27.5	15.0	46.5	5.0	0.89	1.83
7	25.0	27.5	5.0	36.5	5.0	0.87	5.50
8	25.0	27.5	15.0	26.5	5.0	1.55	1.83
9	15.0	20.0	5.0	54.0	5.0	0.45	4.00
10	15.0	20.0	15.0	44.0	5.0	0.78	1.33
11	15.0	35.0	5.0	39.0	5.0	1.00	7.00
12	15.0	35.0	15.0	29.0	5.0	1.67	2.33
13	15.0	27.5	10.0	41.5	5.0	0.88	2.75
14	15.0	27.5	10.0	41.5	5.0	0.88	2.75
15	15.0	27.5	10.0	41.5	5.0	0.88	2.75

Table 2. Initial Alloy Compositions

No	Fe	Mn	Si	C	S
1	15.5	80.0	1.50	3.00	0.08
2	17.0	80.0	1.50	1.50	0.08
3	17.0	65.0	17.00	1.00	0.08
4	15.0	76.0	3.0	6.0	0.08

Analytical Work

The equilibrated samples were separated to slag and alloy parts which were submitted to Mintek for chemical analysis for the following constituents .
Slag Samples: MnO, CaO, MgO, SiO_2 , Al_2O_3 , FeO and S(slag)
Alloy samples : Mn, Fe, Si, C and S

Results and discussion

The equilibrium reactions which may take place between the slag and alloy phases can be summarized as follows:

$2MnO = 2Mn + O_2$ .....(1)
$\Delta G_{1773}^{\circ} = 487554$ (J/mole)

$SiO_2 = Si + O_2$ .....(2)
$\Delta G_{1773}^{\circ} = 594058$ (J/mole)

$2CO = 2C + O_2$ .....(3)
$\Delta G_{1773}^{\circ} = 534799$ (J/mole)

Partial pressure of oxygen of the system is calculated by using the standard free energy of reaction(3) through the use of P_{CO}=0.423 atm (P_{total}=0.83atm in Johannesburg and volume percent of CO in the gas is actually 50.95%) and a_C=1.0 (due to graphite crucible) resulting in $Po_2=3.17X10^{-17}$atm.

The activity of Mn in the metal phase can be calculated from reaction 1 as :

$$K_{1773} = \frac{(a_{Mn})^2 \times P_{O_2}}{(a_{MnO})^2} \quad \text{.....(4)}$$

a_{MnO} values are calculated from known activity values given in the literature. The Mn activity values less than 0.90 are considered to be within the acceptable range, therefore the experimental data which belong to the corresponding samples are assumed reliable and were used to calculate the distribution ratios of manganese, silicon and sulphur in the slag and alloy phases defined as (Mn)/[Mn] , (Si)/[Si] and (S)/[S], where round brackets refer to the slag phase and square brackets refer to metal phase.

Transfer of Si between slag and alloy phase was found to be the main step in attaining the equilibrium. The slag+alloy samples which had initially high silicon-17% in the alloy and hence low (Si)/[Si] ratio reached to the equilibrium state quicker than the samples which had low silicon-1.5% and high (Si)/[Si] ratio.

The basicity of the slag is defined as $(CaO+MgO)/SiO_2$ in this work. As it is expected, (Si)/[Si] increased whereas (Mn)/[Mn] decreased with increasing basicity of the slag as shown in Figures 1 and 2. Higher CaO and MgO contents of the slag increased the activity of MnO and therefore decreased its content in the slag. (Mn)/[Mn] however reached to a steady value at basicities greater than 1.0. SiO_2 on the other hand had a lower activity with increasing CaO and MgO contents and therefore had higher content in the slag.

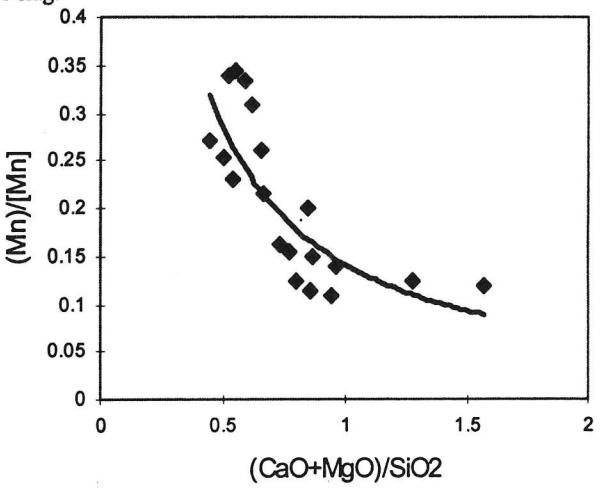

Figure 1. Manganese distribution between slag and alloy phase as a function of basicty ratio

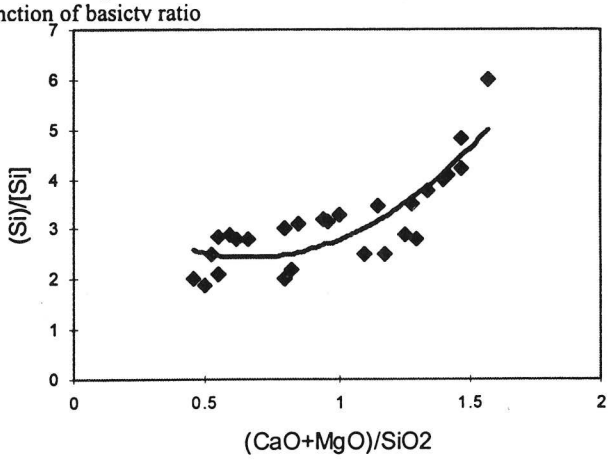

Figure 2. Silicon distribution between slag and alloy phase as a function of basicity ratio.

Carbon content of the alloy phase was found inversely proportional to the ratio of Si/(Fe+Mn) which is obviously due to the solubility of carbon in the alloy which is known as low in the presence of Si and high in the presence of Fe+Mn (Figure 3).

Almost all of sulphur initially present in the alloy was transferred to the slag phase depending on the basicity of the slag as can be seen in Figure 4. CaO present in the slag was probably the main component in transferring S to the slag phase by forming CaS in the slag.

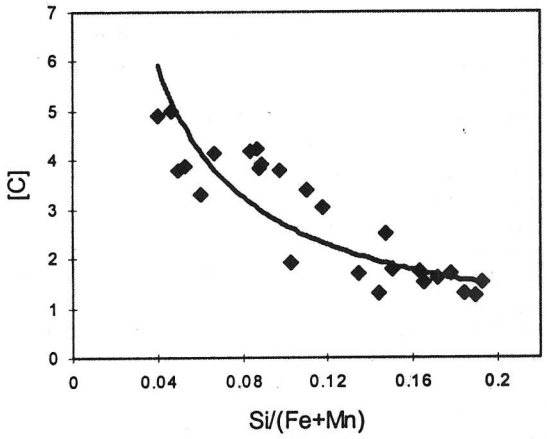

Figure 3. Carbon content of alloy phase as function of the Si/(Fe+Mn)

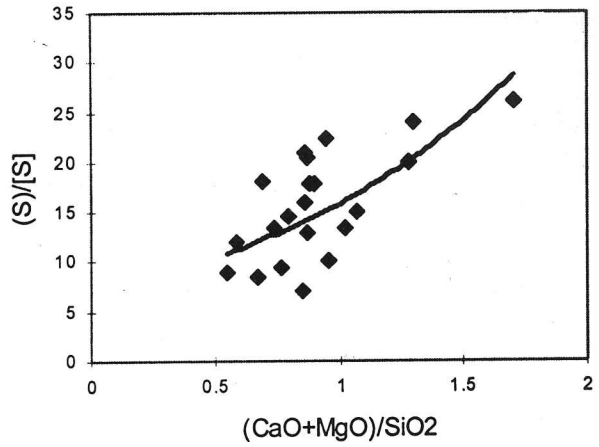

Figure 4. Sulphur distribution between slag and alloy phase as a function of basicty ratio.

Conclusion

1. Transfer of silicon between the slag and the alloy phase was found to be the main step in attaining equilibrium.
2. (Si)/[Si] ratio showed an increase with increasing basicity .
3. (Mn)/[Mn] showed a decrease with increasing basicity.
4. Carbon content of alloy phase was found to be within the medium carbon range changing from about 5.5% to 1.0%, and decreasing with [Si] and increasing with [Fe+Mn].
5. A high proportion of sulphur was transferred to the slag phase.

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