POTASSIUM DISTRIBUTION BETWEEN LIQUID Mn-Fe-C ALLOYS AND MnO-SiO_2-CaO SLAGS

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ABSTRACT

The equilibrium distribution of potassium between liquid Mn-Fe-C alloys and molten K_2O-containing MnO-SiO_2-CaO slags in CO atmosphere were studied experimentally at 1400-1500^oC. Experimental results indicate that potassium preferably goes to the gas phase under reducing conditions. The solubility of K in Mn-Fe-C alloys is negligible. The K_2O content in all the slag samples is lower than those in industrial slags. Carbon plays an important role in the K-distribution equilibria. Potassium oxide is probably reduced to gaseous potassium rather than to metallic potassium in the metal phase. Based on the equilibrium measurements, thermochemical behavior of K in Mn-based alloys was evaluated. The results of the model calculations have been used to explain the experimental observations.

KEYWORDS: *K distribution, liquid Mn-Si-C alloys, MnO-SiO_2-CaO slags, thermochemical modeling.*

1. INTRODUCTION

In the production of ferromanganese alloys, alkaline impurities, such as K_2CO_3 and Na_2CO_3, are charged with raw materials to the furnace. Due to the volatile nature of the alkaline materials, they accumulate in the furnace by internal recycling. The presence and circulation of alkalis lead to inconvenience in the furnace operation and to influence the carbon balance by the increasing coke and energy consumption. It is therefore important to study the potassium distribution equilibria in order to control the alkaline circulation. Because the alkalis are very similar in their thermochemical behavior, only the potassium has been considered in the present study. Sodium should act in a similar manner as potassium in the furnace.

Phase relations in the ternary K_2O-SiO_2-CaO and K_2O-SiO_2-Al_2O_3 systems are well-known [1]. Thermodynamic properties of the K_2O-conatining MnO-SiO_2-CaO-Al_2O_3-MgO system can be reasonably well predicted based on assessed sub-binaries and ternaries [2].

Manganese, iron, silicon and carbon are the key components in the manganese ferroalloys. Thermodynamic properties of the K-bearing Mn-Fe-Si-C alloys are essential to simulate the potassium distribution equilibria. However, very little experimental information exists for K-containing Mn-Fe-Si-C alloys. The solubility of potassium in pure Fe is negligible, according to Massalski [3]. Neither phase diagram nor thermodynamic property data for the Mn-K and Si-K systems have been found in the literature [3]. Furthermore, the influence of carbon on the solubility of K in the metal phase has not been defined yet. In order to get an estimate of the potassium content in Mn-Fe-Si-C liquid solution, it was necessary to employ a theoretical estimation. The Miedema model [4] has been chosen to estimate the solubility of K in Mn, Fe and Si.

2. THEORETICAL ESTIMATION

The Miedema model is one of the most important achievements in the field of alloying theory. From the basic properties of pure components, the formation enthalpy of any binary alloy can reasonably predicted except for those containing O, S, Se and Te. In general, the predicted values of enthalpy of formation are in rather good agreement with the measured values within an accuracy ±8 kJ/mol. It was also found [5] that the model can predict successfully the sign of the enthalpy of formation (endothermic or exothermic reaction) for about 500 binary alloy systems.

The enthalpy change of an *i-j* binary, ΔH_{ij}, can be estimated [6] in term of the basic properties of element *i* and *j*:

$$\Delta H_{ij}^{M} = h_{ij}\frac{X_i X_j[1+a_i X_j \Delta\phi][1+a_j X_i \Delta\phi]}{V_i^{2/3} X_i[1+a_i X_j \Delta\phi]+V_j^{2/3} X_j[1+a_j X_i \Delta\phi]} \tag{1a}$$

And

$$h_{ij} = \frac{2pV_i^{2/3}V_j^{2/3}[\frac{q}{p}(\Delta n_{WS}^{1/3})^2-(\Delta\phi)^2-\rho\frac{r}{p}]}{(n_{WS}^{1/3})_i^{-1}+(n_{WS}^{1/3})_j^{-1}} \tag{1b}$$

where X_i and X_j are the mole fraction of components *i* and *j* respectively, V_i is the molar volume of the solute *i*, n_{WS} is the electron density, ϕ is the electronegativity and Δ denotes the difference between solute and solvent. The empirical constants, *p*, u_i, *a*, and (*r/p*), are dependent on the elements and the type of alloy. The partial enthalpy of *i*, $\overline{H}_i^o$, in an *i-j* solution is readily arrived [6]:

$$\overline{H}_i^o = \frac{2\ p\ V_i^{2/3}\left(1+u_i(\phi_i-\phi_1)\right)\left\{9.4\left(\Delta n_{ws}^{1/3}\right)^2-(\Delta\phi)^2-a(r/p)\right\}}{\left(n_{ws}^{i}\right)^{-1/3}+\left(n_{ws}^{1}\right)^{-1/3}} \tag{2}$$

When the enthalpy of mixing has been obtained, the excess Gibbs energy can be estimated under the assumption: $\Delta H_{ij}^{M} = \Delta G_{ij}^{E}$, which implies that potassium in binary solutions with Fe, Mn and Si behaves regularly. The solubility of potassium in manganese, iron and silicon is then obtained by assuming unity activity of K:

$$x_K^{sat} = \exp\left(\frac{-\overline{H}_K^o}{RT}\right) \tag{3}$$

where the partial molar enthalpy of potassium at infinite dilution, $\overline{H}_K^o$ can be obtained from Eq.(2).

Table 1 shows the calculated potassium solubility in liquid Mn, Fe and Si.

Table 1 : Solubility of potassium in liquid Mn, Fe and Si

Solvent-solute	Fe-K	Mn-K	Si-K	C-K
$\overline{H}_K^o$ **(kJ/mol)**	431	557	97	-120
ppm K at 1400°C	2.4E-08	2.8E-12	1300	-
ppm K at 1500°C	1.4E-07	2.7E-11	1900	-

The calculated solubility of potassium in pure liquid Fe is negligible. That is in good agreement with experimental observation [3]. Since Mn is chemically similar to Fe, the solubility of potassium in pure liquid manganese should also be negligible.

The calculated solubility of potassium in liquid silicon is relatively higher at temperatures of interest (1400-1500°C). Using a similar procedure one may also estimate the relative partial molar enthalpy of potassium at infinite dilution in a hypothetic liquid C-K solution to be -120 kJ/mole at 1500°C. Hence, it is reasonable to assume that carbon in FeMn alloys may play a role to "catch" potassium. Increasing Si contents in the metal phase may have the same effect as carbon. The theoretically estimated results can be used to explain the K contents in commercial FeMn and SiMn alloys.

3. EXPERIMENTAL

3.1. Materials

The chemicals used in the present study are given in table 2. These materials were used to prepare master alloys and slags for the equilibrium measurements.

Two K_2O-containing synthetic slags were prepared by melting the mixture of chemicals in graphite crucibles in Ar atmosphere. A Balzer induction furnace was used. The slag samples were cast into an iron mould immediately after complete melting in order to avoid reduction of the potassium oxide by graphite followed by evaporation of potassium. Two master alloys with fixed Mn/Fe ratio (Mn/Fe=6) were also prepared using the same equipment as for the slag samples.

Table 2: Chemicals used in this study

Chemicals	Quality	Manufacturer
SiO_2	pro analysis	Merck, 1.07536
MnO	>99%	Alfa, 011870
CaO	>97%	Merck, 1.02109
K_2CO_3	>99%	Riedel-de Haën AG, 12611
Mn	>99%	Merck, 1.03819
Fe	>99.5%	Merck, 1.12237
CO	99.0%	AGA Norgas AS
Ar	99.99%	AGA Norgas AS

The premelted slag and metal samples were crushed to fine powders (less then 150 micron) for chemical analyses and for the equilibrium measurements. Chemical analyses of the premelted samples are listed in table 3. The first premelted alloy sample contained abnormally high oxygen content and the carbon content was lower than anticipated. The sample might have been contaminated in the preparation. The premelted alloy-1 and slag-1 samples were used for the first three experiments and alloy-2 and slag-2 for the last experiment only.

Table 3: Chemical analyses of the premelted alloy and slag samples

Element	Mn	Fe	Si	Ca	C	O	K	Sum
Alloy-1	80.8	13.9	< 0.01	0.0065	4.46	1.0	<0.002	100.2
Alloy-2	79.0	13.5	0.02	0.0	7.42	0.17	0.00047	100.1
	MnO	FeO	SiO_2	CaO			K_2O	
Slag-1	37.8	0.04	28.3	27.4			6.1	99.6
Slag-2	36.8	0.26	30.9	28.6*			3.4	100.00

* estimated based on mass balance

3.2. Apparatus

The experiments were conducted in a graphite resistance furnace. The experimental set up for equilibration measurement is schematically shown in figure 1. The crucible was placed at the end of a molybdenum rod. After the equilibrium measurements, the Mo-rod was lowered so that the crucible was placed in the quenching chamber. The quenching valve was closed and the crucible was cooled in a stream of argon. The white arrow in figure 1 indicates the position of the sample in the furnace. "0 mm" refers to the centre of the furnace. The temperature was measured and controlled by two Pt/Pt-10%Rh thermocouples, one in the centre of furnace and another just above the graphite crucible. The latter was used to measure and control the temperature profile. Figure 2 illustrates the temperature profile under the current experimental conditions.

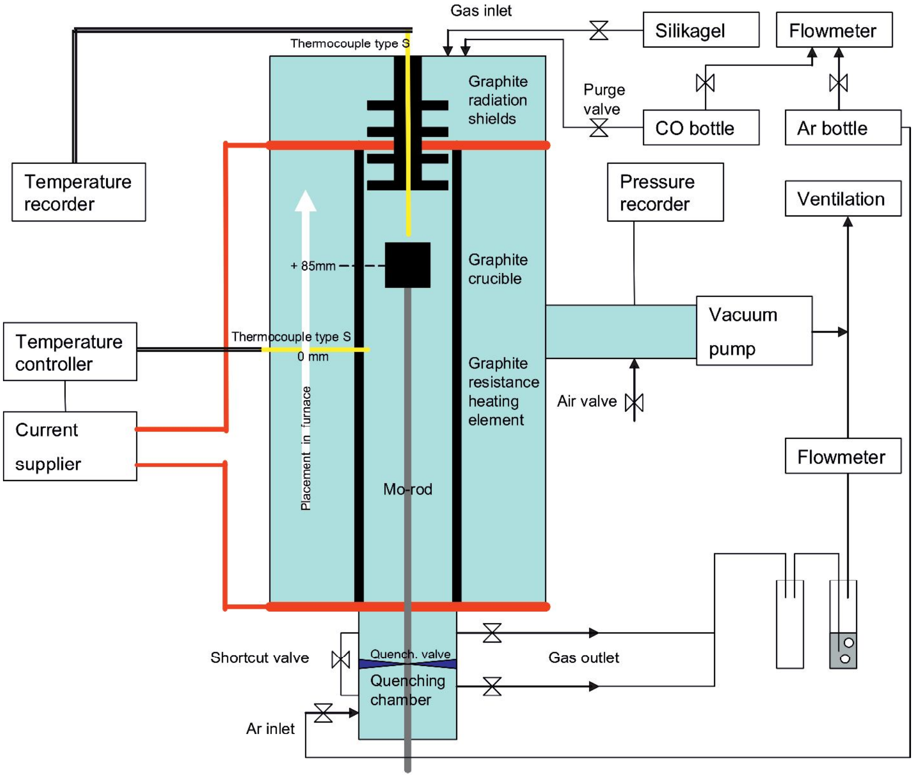

Figure 1: Sketch of the equilibration apparatus

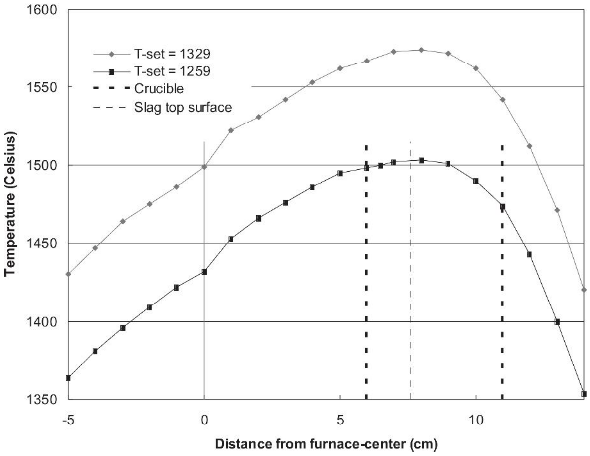

Figure 2: Temperature profile in the furnace

3.3. Procedure

The pre-melted alloy and slag were placed either in graphite crucible (inner height 50 mm and diameter 40 mm) or in MnO crucible (inner height 56 mm and diameter 36 mm). The slag/metal ratio is an important parameter. In the first and second run with graphite crucibles, the slag/metal weight ratio was around 0.8. When MnO crucibles were used, the slag/metal ratio was changed to about 2.0 in order to ensure maximum content of potassium in the metal phase. The charged crucible was placed at the end of the rod and raised to the reaction zone. A Ta-rod was used in the first measurement, but it was partially melted down. In the later experiments, a molybdenum rod was used. When MnO crucibles were applied, an outer graphite crucible was used as protection in case of slag and metal leakage.

The system was sealed and evacuated by a rotary pump. CO gas was then gradually introduced into the system. The CO gas flow rate was controlled at 0.1 L/min. The heating rate was controlled at 15 ^{o}C/min for the first and second run of experiments. In the later measurements, the heating rate was reduced to 10 ^{o}C/min in order to prevent the MnO crucible from cracking. The samples were held at desired reaction temperature (normally 1500^{o}C) for 2 hours. The crucible was then lowered to the quenching chamber. The quenching valve was then closed and the sample was cooled in Ar atmosphere.

Metal and slag were carefully separated from the crucible. The samples were pulverized and submitted for chemical analysis or prepared for microanalysis.

3.4. Chemical analysis and microanalysis

The chemical analyses were conducted either at the SINTEF Chemistry laboratory, at the Eramet laboratory in Sauda or at LabNett in Skien. The elements Fe, Mn and Si in the slag phase were determined by X-ray fluorescence spectroscopy, and wet chemical analysis were applied to determine Fe, Mn and Si in the metal phase: dichromate titration for Fe contents; redox titration with potassium permanganate for Mn contents and gravimetric analysis for Si. The elements K and Ca in both metal and oxide phases were determined by inductive coupled plasma (ICP). Carbon and oxygen contents were analyzed by combustion technique (C: Leco TC-136, O: Leco CS-200). The potassium contents were analyzed twice in order to get reliable data. Only the average values are presented in this paper.

In addition to chemical analyses, samples from the second experiment with MnO crucible were also examined by scanning electron microscope (SEM) and X-ray imaging microanalysis.

4. RESULTS AND DISCUSSION

4.1. Results

The first measurement was not successful due to the partial melt down of the Ta-rod during the experiment. According to the temperature profile given in figure 2, the actual reaction temperature of this measurement was between 1400-1500^{o}C. Nor were the experiments with MnO crucibles successful since the crucibles cracked during the measurement. This happened although the heating rate was adjusted to be relatively slow. Parts of liquid metal and slag had leaked out into the graphite crucible through cracks in the wall and bottom of the MnO crucibles.

Even though the experiments were not completely successful, some typical results are listed in table 4 for reference. The initial and final compositions of slag samples are shown in figure 3. The MnO-SiO_2-CaO ternary system is used to represent the experimental results since the contents of K_2O and FeO were small. It is worth noticing that the "path" of composition change in the second experiment (graphite crucible) is mainly due to reduction of MnO in the slag phase. The slag becomes MnO-saturated when MnO crucibles are applied.

Table 4: Results of typical experiments

	Fe	**Mn**	**Si**	**Ca**	**K**	**O**	**C**	**Note**
Metal-2	13.8	78.9	0.02	0.0	0.00285	0.22	7.4	1500°C**
Metal-4	12.4	79.9	0.03	N.D.	0.00165	0.73	7.22	1500°C**
	FeO	**MnO**	**SiO_2**	**CaO**	**K_2O**	**C**		
Slag-2	0.2	41.6	29.4	25.1	0.010	0.12		Graphite*
Slag-4	2.8	60.0	18.3	16.7	0.017	1.6		MnO*

* crucible materials

** experimental temperature

N.D. not determined

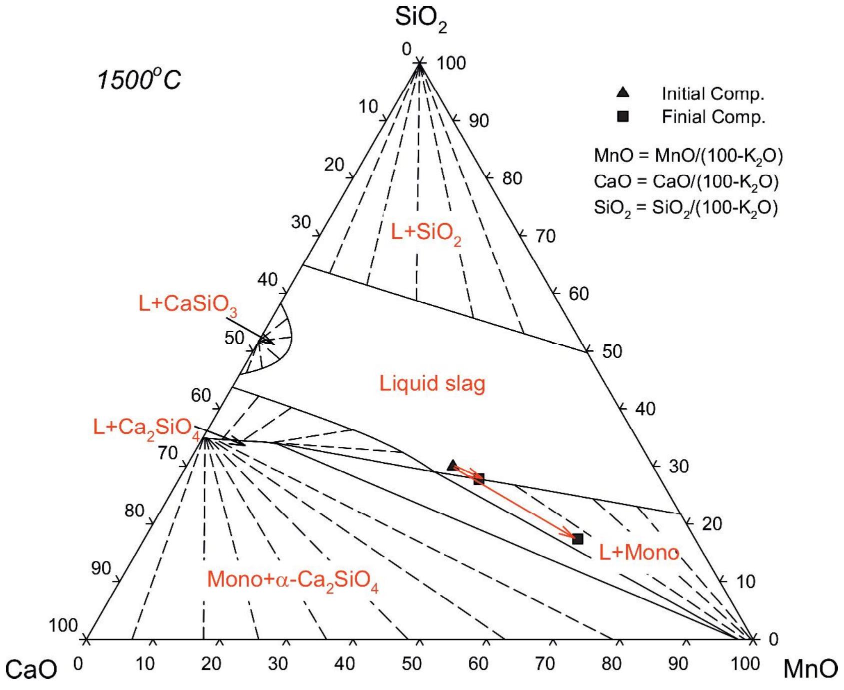

Figure 3: Typical experimental results

X-ray images of both metal and slag samples from experiment 2 have dark and bright areas. The results of scanning electron microscopy (SEM) indicate higher carbon contents in the dark slag area. Small amounts of K were also detected in the same area. This implies that potassium carbides are formed during the measurement. No potassium was detected in the bright area of the slag sample. The SEM images suggest that inhomogeneity exists in the slag sample.

4.2. Discussion

The distribution coefficients of potassium between gas, liquid slag and metal phases have been estimated from the present experimental results and are shown in figure 4. The estimations were made based on the mass balance of the experiments. As figure 4 shows, potassium goes almost completely to the gas phase when the graphite crucible is used. The graphite crucible acts as carbon source in this case. Potassium oxides in slags may be reduced according to:

$$(K_2O) + C_{gr.} = 2K_{(g)} + CO_{(g)} \quad (4a)$$

$$(K_2O) + C_{gr.} = 2\underline{K} + CO_{(g)} \quad (4b)$$

Potassium oxide may also be reduced by the carbon monoxide:

$$(K_2O) + CO_{(g)} = 2K_{(g)} + CO_{2(g)}(4c)$$

where parentheses denote the slag phase and underscored the alloy phase.

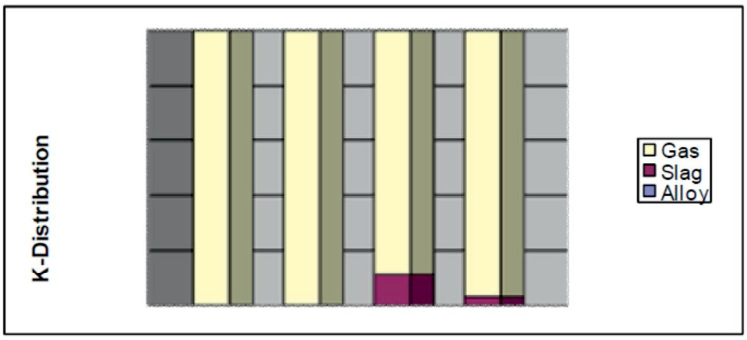

Figure 4: Potassium distribution among gas/slag/metal phases

The Gibbs energy changes of the three reactions above are shown in figure 5 as function of temperature. Obviously, reaction (4a) is the most favorable to take place in the present case. The predominant reaction product, $K_{(g)}$, will further react with carbon materials to form potassium carbides:

$$K_{(g)} + n"C" = KC_n \ (n = 4, 8, 16, 24, 36, 40, 48, 60) \ [3] \quad (5)$$

This was confirmed by the SEM microanalysis of samples from the second experiment.
When the MnO crucibles were used, the slags became MnO-saturated. Only the carbon dissolved in the original metal phase could act as reactant to reduce the potassium oxides:

$$(K_2O) + \underline{C} = 2K_{(g)} + CO_{(g)} \ (\text{carbon activity} < 1.0) \quad (4d)$$

The carbon activity will be reduced gradually during the reduction process. The Gibbs energy changes of eq.(4d) is less negative then of eq.(4a) (figure 5). Consequently the reduction of potassium oxide will be restrained to some extent. Although the MnO crucible was cracked in the experiment, it still prevented direct contact between slag and carbon.

The industrial FeMn slags contain typically 2-3 wt % of K_2O. However, the present experimental results have shown that almost no potassium is left in the metal and slag phases. The current experimental apparatus is a semi-closed system and is able to exchange matter with the surroundings via the gas phase. Since most of the potassium goes to the gas phase (eq. 4a) and leaves the furnace, the partial pressure of potassium inside furnace will hardly be saturated. According to equilibrium calculations based on the FACT slag and pure substance thermochemical databases [10], a gas mixture with potassium pressure higher then 0.02 atm would be required to equilibrate with a 2% K_2O-35 % MnO-22 % CaO-38% SiO_2 slag. It is estimated that the partial pressure of potassium in laboratory furnace was lower then the equilibrium value, being around 10^{-5}

atm under the experimental conditions. In order to simulate industrial operations, a closed apparatus might be installed for investigations of potassium circulation.

Temperatures in the range of 1400-1500°C seem to have no virtual influence on the K-distribution equilibria. This suggests that the reduction of K_2O is fast at 1400-1500°C.

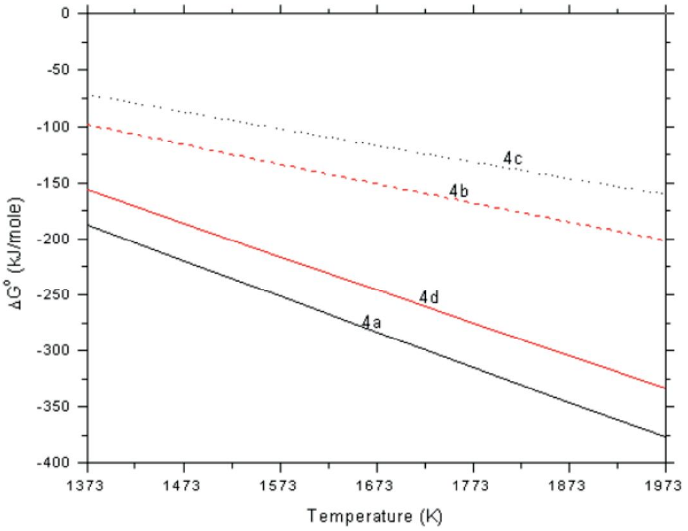

Figure 5: Gibbs energy changes of reduction K_2O

5. CONCLUSION

The equilibrium distribution of potassium between liquid Mn-Fe-C alloys and molten K_2O-containing $MnO-SiO_2-CaO$ slags in CO atmosphere have been studied experimentally. Four measurements were carried out, two experiments with use of graphite crucibles and two with MnO crucibles. The following results have been obtained:

– All experiments indicate that potassium preferably goes to the gas phase under the present reducing conditions.

– The Miedema semi-empirical model was first employed to predict the solubility of K in liquid Mn, Fe and Si. The calculation results have been used to explain the experimental observations.

– The K_2O contents of all slag samples are lower then those of industrial slags. The reason is that the experimental system does not prevent gaseous species from leaving the furnace.

– Carbon plays an important role in the K-distribution equilibria. Potassium oxide is preferably reduced to gaseous potassium, rather than to metallic potassium in the metal phase.

– The solubility of K in Mn-Fe-C alloys is negligible. This implies that a thermochemical model based only on the binary parameters is able to give good description of the potassium behaviour in Mn-based ferroalloys.

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