Reduction Kinetics of MnO-Saturated Slags

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Summary

The kinetics of the MnO reduction in FeMn slag has been studied, mainly focusing on the reduction in the two phase area, where the slag contains a solid MnO phase as well as a liquid oxide phase.

Quaternary $MnO-SiO_2-CaO-Al_2O_3$ slags were used, with Al_2O_3/SiO_2 ratios equal to 0.25 and 0.5. Three basicities were chosen $(CaO/(Al_2O_3+SiO_2))$: 1/3, 2/3 and 1. Initial slags contained approx. 70 wt.% MnO. More than 30 individual experiments were carried out using a weighing technique in a thermobalance apparatus. Most experiments were carried out for 10 hours. The reaction temperatures were 1450 °C, 1500 °C and 1550 °C. The gas atmosphere was CO. Graphite crucibles were used in all experiment, therefore the manganese alloys produced were carbon saturated.

The temperature influences the MnO reduction rate to a large extent. The reduction rate is dependent on the basicity. In the two phase area increasing basicity gives decreasing reduction rate. The slag basicity has the opposite effect in the homogeneous slag area. The Al_2O_3/SiO_2 ratio seems to be of little influence. The activation energy was calculated for the different slag compositions, and generally found to be approx. 370 kJ/mole in the two phase range.

Introduction

High carbon ferromanganese is produced in electric submerged arc furnaces. The raw materials are blends of manganese ores and fluxes and carbonaceous reducing agents. Typical fluxes are quartzite, limestone and dolomitic limestone. The upper part of the submerged arc furnace is a prereduction zone where the materials are in the solid state. In this zone the higher oxides of manganese are reduced to MnO by the gas formed in the lower part of the furnace. As the charge materials reaches the high temperature zone, the ore will melt down and the reduction to Mn takes place. This zone has a stoichiometric surplus of carbon and is called the coke bed zone. The reactions taking place in the different zones of the furnace have been discussed earlier by Tangstad et al. [1].

Optimum operation of a ferromanganese furnace occurs when the power consumption is low and the furnace is operated on a stable and high load. While the power consumption is determined mainly by the reactions of the prereduction zone, the stability of the operation is determined by the reactions in the coke bed zone. The main reaction in the coke bed zone is the reduction of MnO in the slag with coke:

$$MnO_{slag} + C_{coke} = Mn_{metal} + CO_{gas} \quad (1)$$

The aim of this investigation has been to investigate the kinetics of this reaction. Previously Skjervheim et al.[2] investigated the reduction kinetics of slags with less than 45% MnO. In the high carbon ferromanganese process the initial charge will usually contain between 70 and 80% MnO. For a high MnO slag practice this slag is reduced to typically between 30 and 40% MnO. The present investigation will focus on the reduction of synthetic slags initially containing about 70% MnO. The main components of ferromanganese slags are MnO, MgO, CaO, Al_2O_3 and SiO_2. This study is focused on the quaternary system $MnO-CaO-Al_2O_3-SiO_2$.

The slag system and the reduction path

When the oxide materials melt down, the slag will contain a solid MnO phase in coexistence with a liquid [3]. As the reduction proceeds the solid MnO phase will be completely consumed when the total composition reaches the liquidus composition. Knowledge of the liquidus composition is important for evaluation of slag characteristics, such as viscosity and activity of MnO in the slag; and thereby the kinetics of the MnO reduction.

The main components of ferromanganese slags are MnO, MgO, CaO, Al_2O_3 and SiO_2. In the phase diagram below, one apex represents the sum of the acid oxides $(SiO_2+Al_2O_3)$ in a given ratio, one apex represents the sum of unreducable basic oxides such as CaO+MgO, also at a given ratio, and the last corner represents MnO. The liquidus relations for the systems $MnO-SiO_2-CaO$, $MnO-SiO_2-Al_2O_3$ and $SiO_2-Al_2O_3-CaO$ are known [4]. By combining these diagrams we are able to estimate the liquidus compositions of the quaternary system $MnO-CaO-Al_2O_3-SiO_2$ where the Al_2O_3/SiO_2 ratio is fixed. Figure 1 shows the estimated liquidus lines for slags with $Al_2O_3/SiO_2 = 0.25$ at 1500 °C.

Three reduction paths are shown in Figure 1. Because, practically speaking, only MnO is reduced, the reduction path will follow a straight line originating from the MnO corner through the initial charge composition, as illustrated in the figure. This charge composition, and therefore also the reduction path, will have a fixed slag basicity. The basicity may be defined as the classical lime basicity, $(CaO+MgO)/SiO_2$, or other basicity concepts e.g. $(CaO+MgO)/(SiO_2+Al_2O_3)$, or in our case $CaO/(SiO_2+Al_2O_3)$.

Curves representing complete slag-metal equilibrium (1450, 1500, 1550 °C and $p_{CO} = 1$ atm.) are also shown in the diagram. A curve showing slag compositions in equilibrium with a Mn-Si-C_{sat} alloy containing 1% Si is also included. These curves are reproduced from Weizhong Ding [5, 6]

The solid MnO phase will be completely consumed when the liquidus line is reached, and equilibrium is established when/if the equilibrium line at the current temperature is reached.

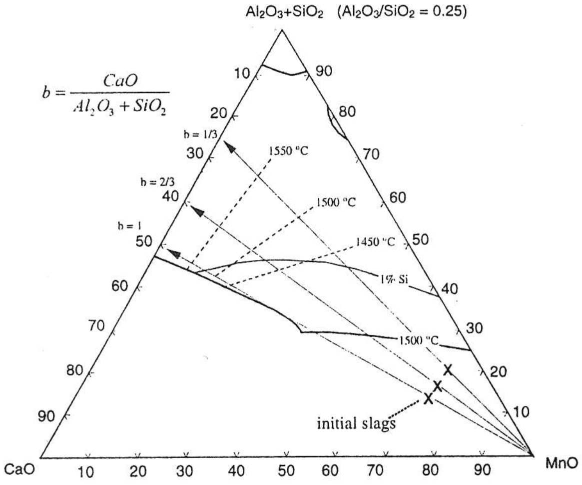


Figure 1. Diagram showing reduction paths for different basicities. Liquidus lines are estimated. Equilibrium curves are reproduced from Weizhong Ding [5, 6].

Experimental

Materials and analysis

Two master slags were prepared, with Al_2O_3/SiO_2-ratios 0.25 and 0.5. The master slags were melted at 1350 °C in a graphite crucible. The molten slag was then cast on a steel plate, and finely ground. The master slags would contain 55-60 wt.% MnO.

Before each experiment, MnO and CaO were added to the slag to give the required composition of each initial slag. Basicities ($b = CaO/(Al_2O_3+SiO_2)$) 1/3, 2/3 and 1 were used. The initial MnO content in the slag was 72 - 73%. The graphite crucible acted as reductant. There was no initial metal.

The final slags were analysed chemically at Molab AS. In the cases where the product slags were homogeneous glass, they were also analysed by an Electron Probe Micro Analyser.

Apparatus

The experimental set-up is shown schematically in Figure 2. Mainly, it can be divided in four parts: a vertical furnace, a balance, a temperature control device and the gas supply system.

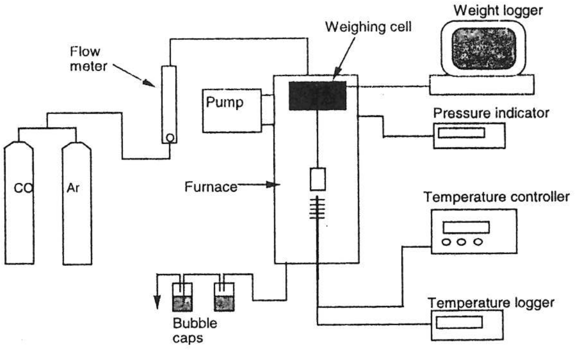


Figure 2. Schematic illustration of experimental apparatus.

Procedures

The crucible was charged with the initial slag, usually 20 g, and suspended from the balance within the furnace. The furnace was closed and evacuated to approximately 1.5 mbar, and held at this pressure for about 30 minutes. Then CO was supplied until a pressure of approx. 1000 mbar was reached. Then the CO gas flow was set at approx. 0.4 l/min. The thermocouple was placed approx. 1 cm below the crucible. The temperature controller was adjusted to maintain a stable reaction temperature.

The temperature was raised quickly to the required temperature (approx. 15 min.). The slag was held a few minutes at ~1350 °C, until the weight became stable, and all weight losses due to volatiles and calcination of the crucible were finished. The time was set to zero when the reaction temperature was reached.

The experiments were usually run for 10 hours, though there were some variations. The temperature and weight loss was recorded at 60 seconds intervals. The recorded weight loss was later corrected due to side reactions, which has been determined to be mainly some evaporation of manganese.

When the experiment was finished, the CO flow was stopped, and the slag was cooled down in a flow of argon. After approx. 30 minutes, the crucible was removed from the furnace.

Results and Discussion

The influence of the slag composition and temperature.

The experiments were performed with slags having Al_2O_3/SiO_2-ratios of 0.25 and 0.5. Generally, the results indicate that the Al_2O_3/SiO_2-ratio has little influence on the reduction rate, as shown in Figure 3. This corresponds with the results of T.A. Skjervheim [7].

Experiments were carried out with three different basicities: $CaO/(Al_2O_3+SiO_2)$ = 1/3, 2/3 and 1. The results are consistent; increased basicity gives a decreasing reduction rate in the two phase region. Figure 4 shows the weight losses at 1500 °C for a slag with Al_2O_3/SiO_2 ratio 0.5 at basicities 1/3, 2/3 and 1. When the slag composition reaches the completely liquid state, the opposite occurs: increasing basicity increases the reduction rate. This agrees

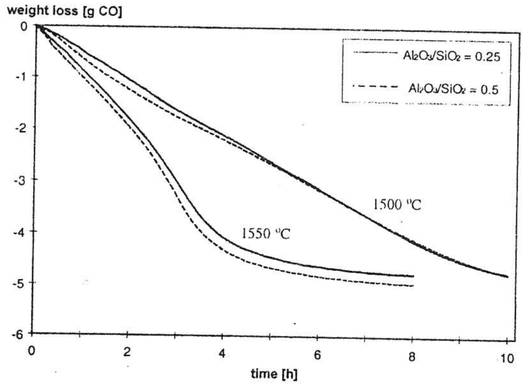


Figure 3. Weight loss [g CO] at 1500 and 1550 °C (b = 1). The Al_2O_3/SiO_2-ratio has little influence on the reduction rate.

with previous studies by T.A. Skjervheim [7]. Figure 5 shows the weight loss during the late stages of the experiments shown in Figure 4. Now "zero" time is chosen to be when the MnO content in the slags are 45%, and the amount of slag approx. 10 g. The weight loss during in the first 4 hours of T.A. Skjervheim's Experiment 68 is also shown. This experiment was performed with a similar slag (Al_2O_3/SiO_2=0.4, b=0.43, initial MnO cont. 45%) at the same temperature. The results seem to agree very well. It has to be noted that Skjervheim's initial amount of slag was 20 g. Therefore, one might have expected a slightly higher weigh loss than in the present study.

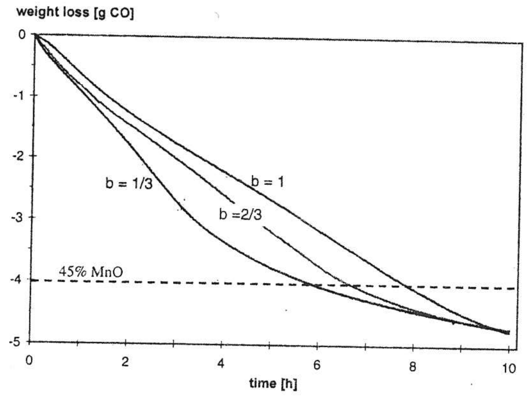


Figure 4. Weight loss [g CO] at 1500 °C (Al_2O_3/SiO_2 = 0.5). The weight loss rate decreases with increasing basicity.

Figure 6 shows weight losses at various temperatures, all for the same initial slag composition. At 1450 and 1500 °C the reduction rate is approx. constant in the two phase range. At 1550 °C the rate is approximately constant early in the experiment, followed by an increased reduction rate after approx. 1 hour. The reason is uncertain, but it might have something to do with mechanisms like slag foaming, wetting of slag vs. graphite etc... This tendency occurs for all experiments performed at this temperature.

As the curves in Figure 4 and Figure 6 indicates, the reduction can be divided in two ranges; the first range with a faster reduction rate. At high MnO contents, the slag will contain solid MnO in coexistence with the liquid. The activity of MnO in this slag is close to unity, and the reduction rate is high, and approximately constant. As the solid MnO phase is consumed, the activity of MnO will decrease rapidly, and so will the reduction rate. This indicates that the reaction rate is controlled by the MnO activity of the slag.

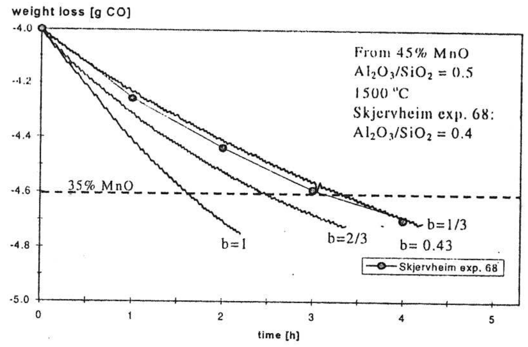


Figure 5. Weight losses in the homogeneous liquid phase. The weight loss rate increases with increasing basicity. Results from one of T.A. Skjervheim's [7] experiments with a similar slag are also shown in the diagram.

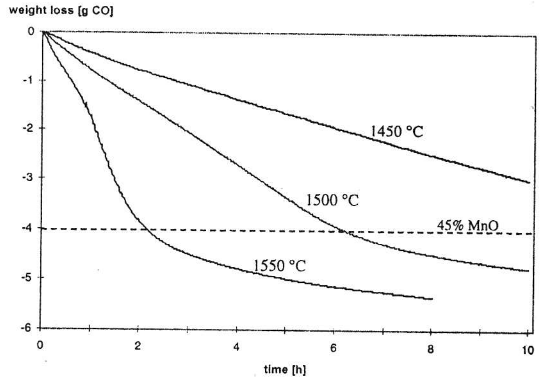


Figure 6. The effect of temperature on recorded weight loss. (Slag: Al_2O_3/SiO_2=0.25, b=2/3)

The slag composition where the reduction rate starts decreasing is the liquidus composition, which may be expressed by its MnO content (MnO(liq.)). These compositions are shown in Table 1.

Table 1. Liquidus compositions %MnO(liq.) according to reduction rate.

	Basicity	Al_2O_3/SiO_2=0.25	Al_2O_3/SiO_2=0.5
1450 °C:	1/3	62 - 63	56 - 57
	2/3	< 56	< 59
	1	< 62	< 64
1500 °C:	1/3	62 - 63	59 - 60
	2/3	51 - 52	47
	1	42 - 43	41 - 42
1550 °C:	1/3	~ 65	
	2/3	~ 54	
	1	~ 43	~ 40

The MnO(liq) composition was never reached at 1450 °C at basicities 2/3 and 1. The liquidus compositions at 1550 °C are more difficult to read out of the curves, due to the character of the curves. The MnO(liq.) composition at 1550 °C is therefore more uncertain than at lower temperatures. The liquidus composition does not appear to be very dependent on the temperature; an increase of 100 °C only increases the MnO(liq.) content by 2-3%. This agrees with the results of Merete Tangstad [8].

The rate constant and the activation energy

The experimental temperatures were 1450, 1500 and 1550 °C. As expected, the reduction rate is heavily dependent on the reaction temperature. This study is focused on the rates in the two phase range, and all rate constants and activation energies calculated are within this range.

The final MnO content of a high carbon ferromanganese slag is previously found to be determined by kinetics, and not by chemical equilibrium [9]. The rate of reaction (1) may be expressed by the following equation:

$$dg/dt = A \cdot k \cdot (a_{MnO} - a_{MnO(eq.)}) \qquad (2)$$

Where dg/dt is the reduction rate e.g. in g/min, A is the reduction area where MnO in the slag is reduced by carbon. k is the rate constant. a_{MnO} is the current activity of MnO in the slag and $a_{MnO(eq)}$ is the equilibrium activity of MnO.

The activity of MnO in the slag (a_{MnO}) will be close to unity as long as the solid MnO phase is present. When the solid MnO phase is completely consumed (%MnO(liq.)), the activity of MnO will decrease rapidly as shown among others by Abraham et al.[10].

The equilibrium activity of MnO, $a_{MnO(eq.)}$ may be calculated from the equilibrium constant, K, given by

$$K = \frac{a_{Mn} \cdot p_{CO}}{a_{MnO(eq.)} \cdot a_C} \qquad (3)$$

The activities of CO and C are unity. The activity of manganese in the carbon saturated iron free system is previously determined by Katsnelson et al. [11] at 1628K, and by Gee and Rosenqvist [12] at 1700K and 1800K.

Table 2 shows the mean value of the rate constant k in the two phase range for each slag composition and temperature.

Table 2. Average k values [g/min cm^2] in the two phase range.

	$\frac{CaO}{Al_2O_3 + SiO_2}$	$\frac{Al_2O_3}{SiO_2} = 0.25$	$\frac{Al_2O_3}{SiO_2} = 0.5$
1450 °C:	1/3	$1.6 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$
	2/3	$1.4 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$
	1	$1.1 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$
1500 °C:	1/3	$4.0 \cdot 10^{-3}$	$3.8 \cdot 10^{-3}$
	2/3	$2.8 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$
	1	$2.3 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$
1550 °C:	1/3	$15.5 \cdot 10^{-3}$	-
	2/3	$9.5 \cdot 10^{-3}$	-
	1	$4.8 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$

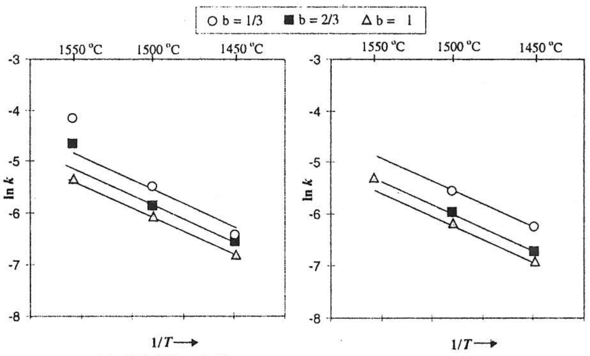
As shown; the rate constant decreases with increasing basicity, whereas the Al_2O_3/SiO_2 is of little influence.

The rate constant k, increasing with increasing temperature, is described by the Arrhenius' equation:

$$k = k_0 \cdot e^{-E/RT} \qquad (4)$$

where R is the gas constant, E is the *activation energy*, and k_0 is the *frequency factor*.

From Arrhenius' equation we can determine the activation energy E of the reaction. Figure 7 shows the graph of ln k against $1/T$ from which the slope E can be determined.



(a) $Al_2O_3/SiO_2 = 0.25$

(b) $Al_2O_3/SiO_2 = 0.5$

Figure 7. Variations of rate constant with temperature .

At 1550 °C and low basicities the k values deviate somewhat from the straight line.

At Al_2O_3/SiO_2=0.25 and $CaO/(Al_2O_3+SiO_2)$ = 1/3 there are some deviations from the main tendency. Excluding this value, the average activation energy is 366 kJ/mole. Merete Tangstad [8], carried out similar experiments with BHP ore, and found the activation energy to be 367 kJ/mole. The results seem to agree very well.

Conclusions

The thermobalance method is a reliable experimental technique when studying reduction rates of liquid slags. However, corrections are necessary due to weight loss caused by side reactions, mainly vaporisation of manganese.

The reduction of MnO takes place in two stages: The first stage in the two phase area, where the slag contains a solid MnO phase as well as a liquid oxide phase, and the second stage where the slag is a homogeneous liquid. In the first stage the rate of reduction is fast and remains approximately constant as the reduction proceeds. In the second stage, the rate of reduction decreases rapidly with increasing reduction. This indicates that the reaction rate is controlled by the MnO activity of the slag.

The reduction rate decreases with increasing basicity in the two phase range. In the homogenous slag area increasing basicity increases the reduction rate. The Al_2O_3/SiO_2 ratio of the slag seems to have little influence on the reduction rate.

The temperature influences the MnO reduction rate to a large extent. The activation energy was calculated for the different slag compositions, and found to be approx. 370 kJ/mole in the two phase range.

Acknowledgements

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