REDUCTION KINETICS OF MANGANESE OXIDE FROM HC FeMn SLAGS

G. Tranell, S. Gaal, D. Lu, M. Tangstad[1] and J. Safarian[1]

SINTEF Materials and Chemistry, Alfred Getz vei 2, NO-7465 Trondheim, Norway
[1]Department of Materials Science and Engineering, NTNU, Trondheim, Norway
E-mail: gabriella.tranell@sintef.no

ABSTRACT

The kinetics of MnO reduction from high carbon ferromanganese slag was investigated using a sessile drop technique at 1600 ºC. The effects of reductant type, ambient atmosphere and slag composition on the MnO reduction were illuminated. Two different types of industrial reductants (ground to a particle size of 44 to 106 micron and pressed to pellets) were used as substrates for small slag droplets of varying composition, which were reacted in a CO or Ar atmosphere with the reaction studied in-situ. The cross sections of the reacted slag-carbon samples were subsequently studied by EPMA to find the extent of MnO reduction as a function of reaction time. It was found that the rate of MnO reduction is affected by both the type of reductant, the ambient atmosphere and the presence of metallic components in the slag. Higher reduction rates were obtained for charcoal than for coke as reductant while a CO atmosphere unexpectedly yielded faster MnO reduction than an Ar atmosphere. It was also found that metal prills in the initial slag will increase the rate of MnO reduction.

1. INTRODUCTION

Over the past decades, considerable effort has been put on understanding the complex MnO and SiO_2 reduction reactions that are involved in producing silicon ferromanganese alloys in submerged arc furnaces from liquid manganese-silicate slags, since these reactions determine the yield of manganese and silicon in the alloy produced.

Put simply, the overall silicon and manganese transfer reactions can be expressed as:

$$(\mathrm{MnO}) + \mathrm{C} \rightarrow \underline{\mathrm{Mn}} + \mathrm{CO(g)} \tag{1}$$

$$(\mathrm{SiO_2}) + 2\mathrm{C} \rightarrow \underline{\mathrm{Si}} + 2\mathrm{CO(g)} \tag{2}$$

where brackets denote slag constituents and underlining denotes the metal phase solution. The thermodynamics for these reactions is reasonably well described in the literature, so that for a given slag composition, amount of slag, temperature and carbon activity, the expected yield of manganese and silicon metal at complete equilibrium may be calculated. Although MnO is reduced to metallic manganese by both solid and solute carbon, SiO_2 can only be reduced by solute carbon or solid carbon in the presence of metallic Fe or Mn (because the formation of Si metal requires a low Si activity). In a system with simultaneous reduction of MnO and SiO_2, the slag/metal exchange reaction of manganese and silicon, which is a combination of reactions (1) and (2), has to be taken into account:

$$2(\mathrm{MnO}) + \underline{\mathrm{Si}} \rightarrow 2\underline{\mathrm{Mn}} + (\mathrm{SiO_2}) \tag{3}$$

This reversible reaction is usually considered to be faster than the carbothermic reactions (1) and (2). Hence, partial slag/metal equilibrium may be established between manganese and silicon. If so, the kinetics of reactions (1) and (2) will be mutually linked through reaction (3) and the overall reduction rates thus limited by the slower carbothermic reduction reaction. In typical silicon ferromanganese alloy production at process temperatures around 1600°C, the thermo-chemistry of reactions (1) and (2) in manganese-silicate slags determine that the MnO reduction will be running very close to equilibrium before the MnO activity in the slag is low enough, i.e. the SiO_2 activity high enough, for the SiO_2 reduction to take place to any substantial degree. Hence, the kinetics of the MnO reduction is important both for the initial and subsequent parts of the alloy production process. The kinetics of the MnO reduction by carbon and the effects of different parameters have been studied by several investigators[1-11]. These studies have mainly been conducted in graphite crucibles, with different metal compositions involving Fe-C, Mn-C and Fe-Mn-C alloys. Several mechanisms for MnO reduction have been proposed. For example, it has been observed that stirring has no effect on the kinetics of MnO reduction, while the reduction rate is extensively sensitive to the temperature. Therefore, it has been concluded that the reaction kinetics are not controlled by diffusion in the bulk of the metal and slag phases, suggesting that the rate of MnO reduction from slag is controlled by chemical reaction[1-10]. But, based on the observation that the gas composition affects the kinetics, it has recently been proposed that MnO reduction is mix-controlled involving both chemical reaction and CO mass transfer in the gas phase[11]. The mechanism of MnO reduction from slags by dissolved carbon in liquid iron is well known[3,5,6,10]. According to this mechanism, MnO is reduced by Fe to produce Mn and FeO at the slag/metal interface. Subsequently, FeO is reduced by CO gas to Fe and CO_2 gas at the slag/gas bubble interface, followed by the regeneration of CO gas via the Boudouard reaction with dissolved carbon at the metal/gas bubble interface. In contrast, the mechanism of MnO reduction by solid carbon and dissolved carbon in liquid manganese alloy is still not well established and more investigations are required.

A few studies have recently been carried out to find the effects of the carbonaceous material properties on the kinetics of the simultaneous reduction of MnO and SiO_2 from silicate slags at 1600 °C[12,13]. It was observed that the reductant type influences the SiO_2 reduction to a larger extent than the MnO reduction. The objective of the present study however is to further investigate relations between the kinetics of the carbothermic reduction of MnO and the type of carbon materials (industrial reductants), the reaction atmosphere and the presence of initial alloy versus no initial alloy.

2. EXPERIMENTAL EQUIPMENT AND TECHNIQUE

In order to study the reactions between solid reductants and slag in-situ, under various experimental conditions, as well as being able to investigate the post-reaction products (slag, metal and carbon), a specially developed sessile drop technique was employed. The sessile drop experiments were carried out in small horizontal graphite element heated furnace. The furnace set-up is illustrated in Figure 1.

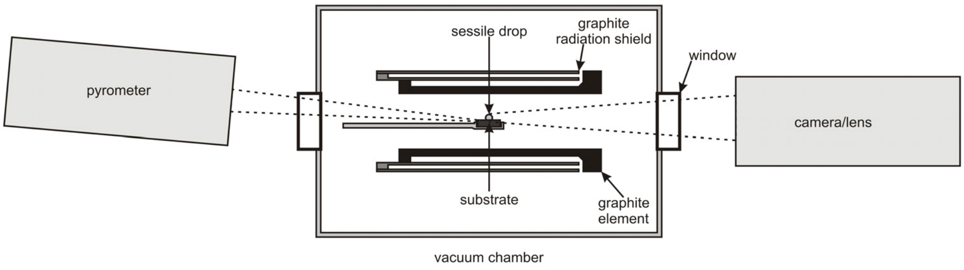


Figure 1: Sessile drop set-up

2.1 Experimental Procedure

As shown in Figure 1, the graphite substrate was located on the graphite sample holder and a 20 mg slag particle was put on the surface of the substrate. The furnace chamber was evacuated initially, and then the furnace was heated up slowly in an argon or CO atmosphere. The furnace was heated to 950 °C in approximately 10 minutes, followed with a rapid heating rate of 120°C/min to the experimental temperature. The temperature was controlled using a Keller PZ40 two-colour pyrometer operating from 900-2400°C focused on the edge of the graphite sample holder. A fire-wire digital video camera (Sony XCD-SX910CR) with a telecentric lens (Navitar 1-50993D) was used to record images from the sample at 960x1280 pixels. In the experiments, drop images were captured every second. When the pre-determined reaction time had elapsed, the furnace was turned off and the sample solidified within a minute. After the samples had cooled down, substrates with slag droplets were cast in epoxy and sectioned vertically through the slag/substrate, revealing the reacted phases and interface for subsequent electron microprobe analysis (EPMA). Two series of reduction tests were performed. In series one, an industrial HC FeMn slag from which the metal particles was removed, was used. In series two, the original metal particles were present in the slag. All experiments were performed at 1600°C. The variables were: type of carbon substrate (industrial coke or eucalyptus charcoal), ambient gas (CO or Ar) and reaction time (15 or 30 minutes).

2.2 Material Preparations

The industrial high carbon ferro-manganese slag was obtained from Eramet Norway in a 10-18mm size fraction. The proximate analysis of the slag obtained is presented in Table 1. For homogeneity, the slag was ground in a tungsten carbide ring-mill to a very fine powder. After initial homogenisation, two different slag types were produced from the starting slag; one containing the "naturally carried-over metal (FeMn prills)" and one without the metallic content. To produce the metal-containing type, the ground slag was fused by rapidly running an oxygen-acetylene torch over the powder. Pieces of the fused slag were subsequently used in the experiments. The second slag-type was produced by melting the ground slag in a graphite crucible in an induction furnace, letting the metallic content settle to the bottom of the crucible, then quenching the slag/metal content and separating the phases. The analysis of the two types of slag are presented in Table 3. For all experiments, fused slag pieces weighing approximately 0.02 grams were used.

Table 1: Composition of industrial HC FeMn slag used for the kinetic experiments, as analysed by wet chemical analysis and XRF

Slag specie	*Content (%)*
MnO	45.6
SiO_2	22.9
CaO	13.9
Al_2O_3	10.5
MgO	4.6
K_2O	1.3
Na_2O	-
BaO	0.8
FeO	0.07
S	0.3
Fe metal	1.9
Mn metal	~ 6

To prepare the carbon substrates, two carbon materials, an industrial coke and eucalyptus charcoal, were ground to fine powder and sieved to a size fraction of +45 –106 μm. These powders were then heat treated in CO at 1600°C for 10 minutes. The "heat treated" powders were subsequently mixed with 3% steric acid (by weight) to achieve some green strength in the produced substrates. Green strength was mainly a problem when producing charcoal substrates but for consistency, the binder was added to all materials. The binder will boil at approximately 383°C and is hence not expected to affect the reactions between substrate and slag at high temperatures. The powder-binder mix was pressed into 10mm diameter, ~1mm thick substrate disks in a pellet press. Prepared substrates were kept in a drying furnace (at 125ºC prior to the experiments in order to avoid moisture absorption. Physical and chemical properties of the carbon materials such as fixed C, porosity, S content, ash content and carbon ordering parameters of the were determined using previously described techniques[12] and are presented in Table 2.

Table 2: Summary of physical and chemical properties of carbonaceous materials used in the present study

Property (unit)	*Industrial Coke*	*Eucalyptus Charcoal*
Fix C (%)	89.36	81.3
Ash (wt%)	10.64	0.43
VM (wt%)	-	18.3
Porosity (%)	27.5	27.3
Average pore diameter (μm)	0.57	0.46
Median pore diameter (area)* (μm)	0.008	0.019
Median pore diameter (vol)**(μm)	26.8	12.4
Total pore area (m^2/g)	1.86	3.86
Skeletal density (g/ml)	1.45	0.90
d (Å)	3.5	3.8
Lc (Å)	23.4	11.5
Approx. fraction amorphous C	0.18	0.69
S content (ppm)	5600	20
CO_2 react. (s^{-1})	$2.78x10^{-5}$	$7.23x10^{-4}$

*pore diameter of pores contributing 50 % of the pore area

**pore diameter of pores contributing 50 % of the pore volume

3. RESULTS AND DISCUSSION

3.1 The Analysed Slag Composition

As described in Section 2, the reacted slag droplets on carbon substrates were mounted, sectioned and subsequently analysed by WDS in the EPMA. A typical sectioned sample is illustrated in Figure 2.

The reacted slag composition was determined by taking an average from 5 analysed points in the slag and used as an indicator of the MnO reduction kinetics for various reaction conditions. As the metal alloy could not always be reliably determined (mainly due to Mn evaporation), these analyses will not be discussed further. The averaged analysed slag composition is given in Table 3. Unfortunately, experience has shown that EPMA, which is the only viable option for this type of analysis, is not optimal when metal is present in the slag as suspended prills - which are often <1μm in size and thus analysed together with the slag (even when the analysis is corrected for the metal analyses). This type of reduced slag will contain less than 0.1% FeO, and the point that some of the samples contain some FeO will indicate that some metal has been analysed. Totals of less than 94% should generally be considered as not sufficiently accurate but indicative of trends in the present work.

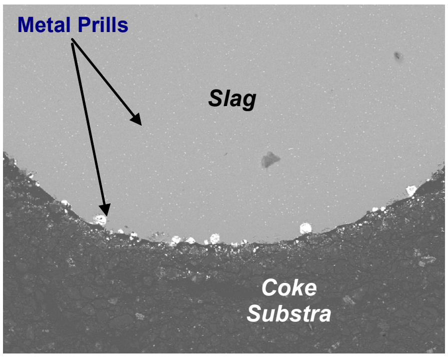


Figure 2: Resulting phases from the reaction between industrial coke and manganese-silicate slag in Ar for 30 minutes. Image illustrating slag droplet on top of coke substrate with metal prills in slag (size < 1 µm) and metal prills at slag/coke interface (5-50 µm)

Table 3: Averaged slag analyses for starting slag and reduced slag (EPMA by WDS)

No	Slag	Substrate	Gas	Time	MgO	MnO	CaO	Al_2O_3	FeO	SiO_2	Total
1	**Initial slag**				**4.9**	**36.5**	**15.1**	**13.5**	**0.1**	**21.2**	**91.3**
2	no metal	Coke	Ar	15	6.1	24.8	17.8	17.1	0.1	31.3	97.2
3	no metal	Coke	Ar	15	6.3	19.5	19.0	17.1	0.2	25.4	87.5
4	no metal	Coke	Ar	30	5.9	28.9	16.9	15.8	0.1	29.2	96.9
5	no metal	Coke	Ar	30	6.9	9.2	21.5	21.6	0.1	31.7	91.0
6	no metal	Coke	CO	15	5.2	24.0	16.2	15.3	0.5	35.9	97.1
7	no metal	Coke	CO	15	6.2	11.1	19.0	17.3	0.1	43.1	96.8
8	no metal	Coke	CO	15	6.1	14.6	18.0	15.9	0.3	34.8	89.7
9	no metal	Coke	CO	30	6.3	4.1	20.5	18.5	0.1	44.9	94.4
10	no metal	Coke	CO	30	6.5	7.4	19.9	17.2	0.4	37.2	88.8
11	no metal	Charcoal	Ar	15	5.5	28.0	17.4	16.0	0.0	29.2	96.1
12	no metal	charcoal	Ar	15	6.5	20.8	19.6	17.3	0.3	26.8	91.2
13	no metal	Charcoal	Ar	30	5.8	24.5	18.3	16.9	0.1	31.0	96.6
14	no metal	Charcoal	Ar	30	6.4	19.4	19.7	18.5	0.1	33.8	97.8
15	no metal	Charcoal	Ar	30	7.1	12.9	21.4	19.2	0.1	29.2	89.9
16	no metal	Charcoal	CO	15	6.4	1.0	27.4	24.8	0.0	35.7	95.3
17	no metal	Charcoal	CO	15	7.0	14.7	20.9	17.6	0.2	28.3	88.8
18	no metal	Charcoal	CO	30	6.4	0.4	27.2	24.2	0.0	35.8	94.1
19	no metal	Charcoal	CO	30	7.5	3.0	25.0	21.5	0.2	30.3	87.5
20	**Initial slag**				**3.5**	**38.4**	**15.5**	**13.4**	**1.4**	**24.3**	**96.5**
21	with metal	Coke	Ar	0	4.5	33.7	16.5	15.2	0.2	24.7	94.8
22	with metal	Coke	Ar	10	5.9	14.4	21.3	21.5	0.2	31.9	95.2
23	with metal	Coke	Ar	15	6.0	12.1	22.6	19.8	0.2	34.2	95.0
24	with metal	Coke	Ar	20	6.4	6.7	23.9	26.2	0.1	32.1	95.3
	with metal	Coke	Ar	30	No slag left to analyse (in both repeated runs)						
25	with metal	Coke	CO	15	5.6	8.2	21.4	17.6	0.2	44.1	97.1
26	with metal	Coke	CO	30	5.8	1.1	24.9	20.2	0.2	43.5	95.7
27	with metal	Charcoal	Ar	15	6.3	1.3	28.4	24.1	0.0	34.8	94.9
28	with metal	Charcoal	Ar	30	5.4	0.1	28.8	24.4	0.1	31.9	90.6
29	with metal	Charcoal	CO	15	4.0	0.2	32.3	26.1	0.0	32.0	94.7
30	with metal	Charcoal	CO	30	5.5	0.1	27.4	23.1	0.1	34.2	90.4

In each series the ratios between the non-reducable oxides, MgO, CaO and Al_2O_3, should be unchanged if the analysis of the sample or the actual composition of the in-going sample is accurate. However, this is not the case as seen in Figure 3. Especially the MgO content seems to be very scattered. The CaO/Al_2O_3 ratio also shows some variation. The scattering is more pronounced in series two, the slags containing original metal prills, which may be expected. In a parallel study to the present, using the identical experimental technique (14), the MnO reduction from synthetic slags on graphite substrates was studied. Repeatable results with very little scatter were obtained and it therefore seems likely that the scatter in the present study may be related to the somewhat unpredictable nature of the industrial slags. The SiO_2 content will theoretically be at the highest during the reduction, when all MnO (or according to the equilibrium data about 5% MnO) is reduced and no SiO_2 is reduced. When the slag has reached a MnO content of 5%, the SiO_2 content will theoretically be 32% and 37% for series 1 (without metal) and series 2 (with metal) respectively. For many of the samples the SiO_2 content is higher than the theoretical possible values, which means that the initial slag analyses or the reduced slag analyses are inaccurate.

In Table 3 all analyses where the SiO_2 content is higher than the possible content, where the sum of elements is low, or where the FeO content is higher than 0.1% is marked with *Italic* formatting. As seen in the table this goes for most of the analyses, and hence, the analyses are assumed to include some metal.

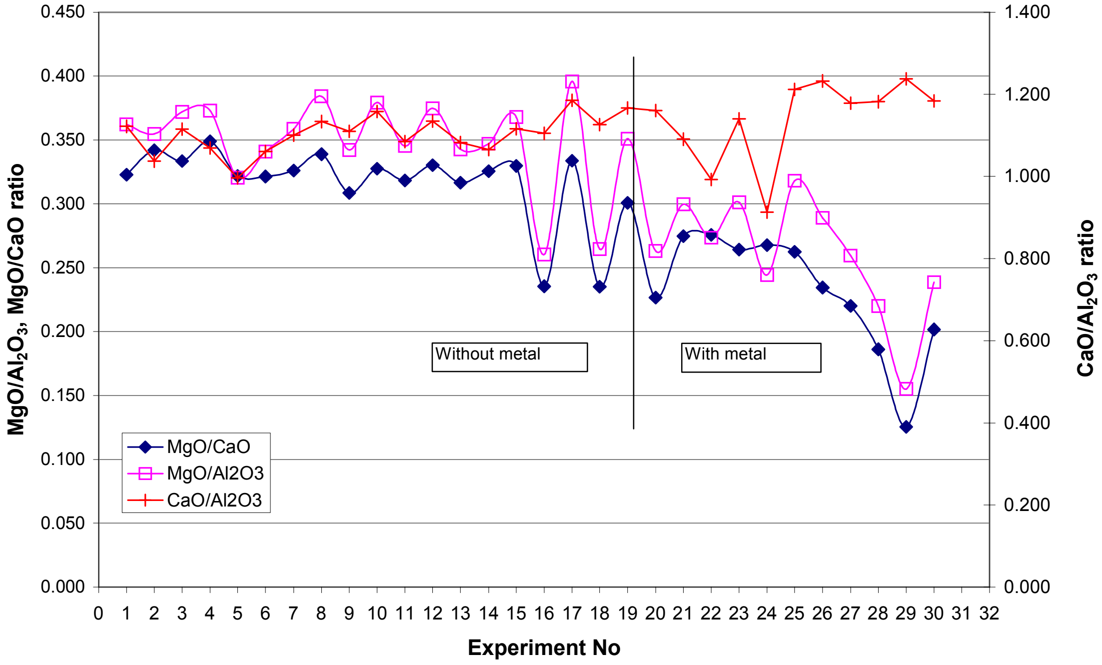
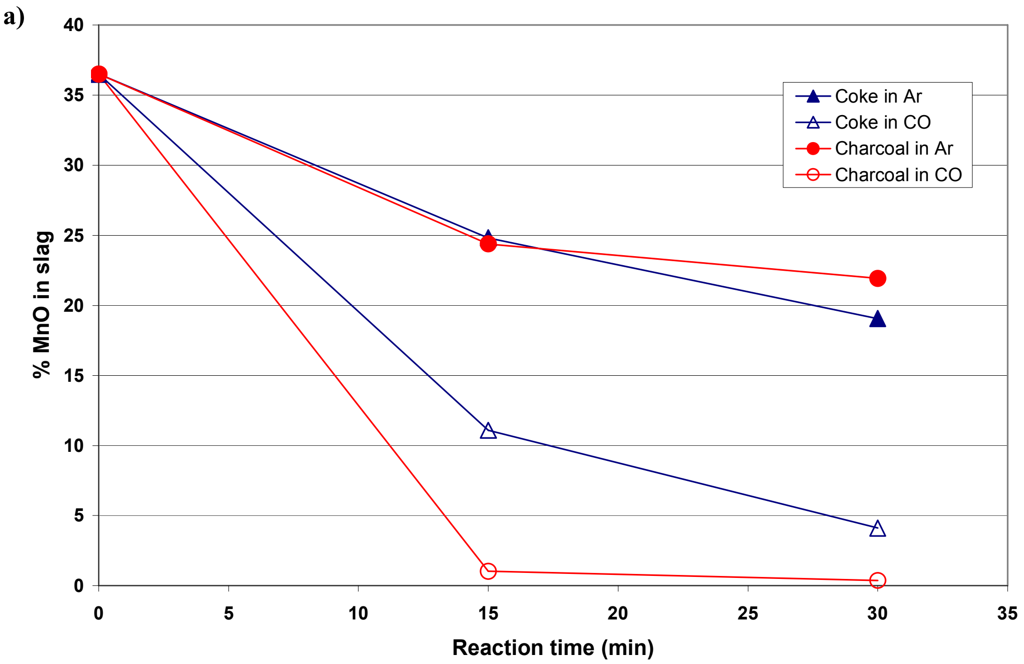


Figure 3: Slag ratios in average slag analyses

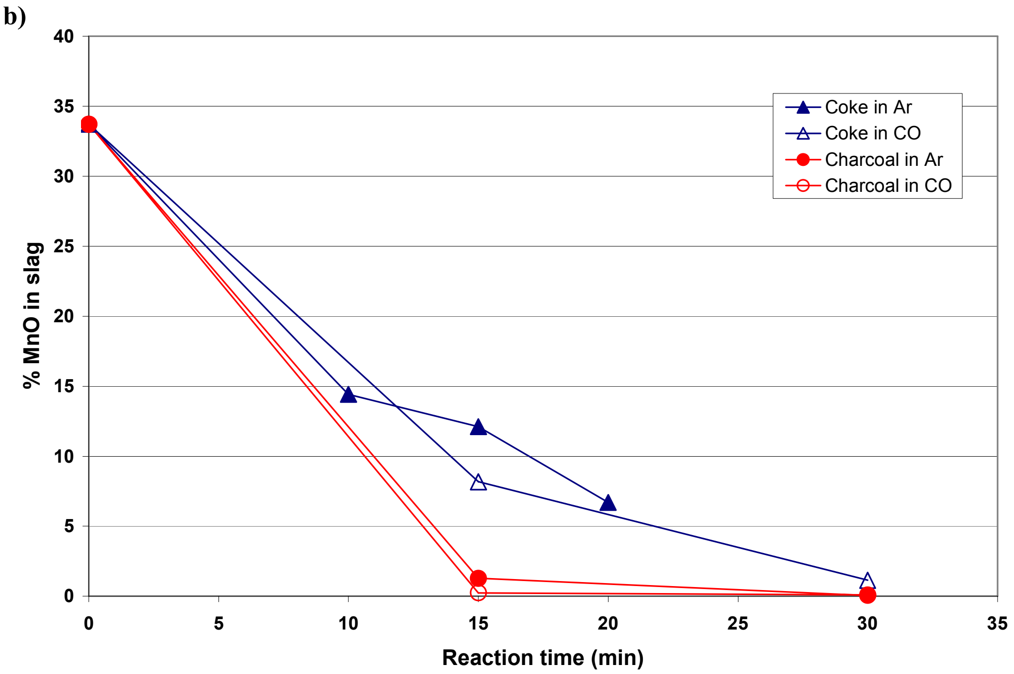
Also, data points with a total elemental analysis sum lower than or close to 90% and/or FeO contents above 0.2 % have been removed from the plots of the data and are marked in grey in Table 3.

3.2 MnO Reduction

Calculating the relative MnO reduction using Al_2O_3 or CaO as tie elements would normally be the chosen procedure when displaying the reduction results. However, the MnO content would show some deviation as the C/A ratio is not consistent. In comparing the MnO reduction, it is in this study hence decided to use the straight forward %MnO in the slag to compare reduction kinetics. If large amounts of silica is reduced, it will affect the percentage MnO as well. However, when the MnO content is below 10%, a reduction from 38 to 25% SiO_2 will only increase the MnO content to 11.5%. This affect is smaller than the total inaccuracy and



*if two parallel analysis points, the value is an average

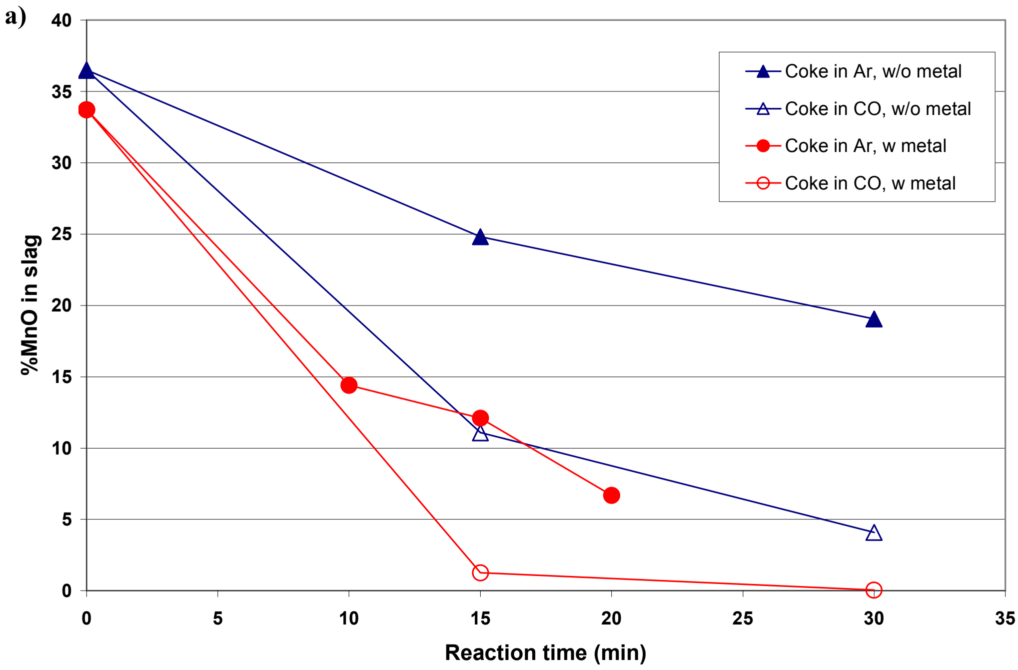


*if two parallel analysis points, the value is an average

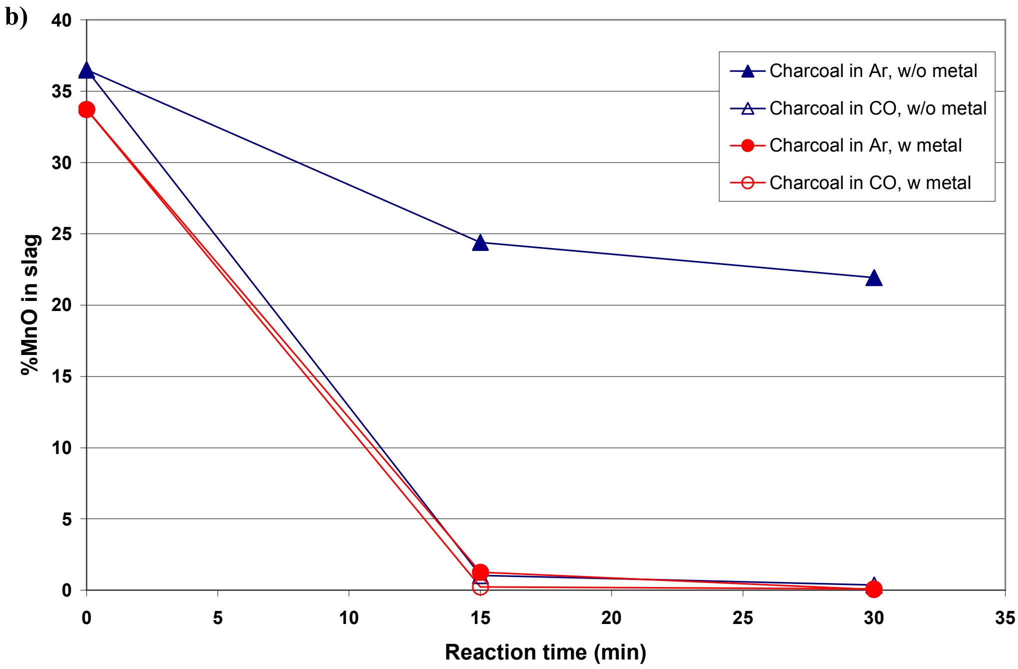
*Figure 4: The concentration of MnO in reacted slag as a function of time for experiments with **a)** no metal **b)** with metal*

hence the MnO reduction may be viewed by the percentage MnO. In Figure 4, the link between MnO reduction rate and gas atmosphere is illustrated.

As can be seen from Figure 4, for all parallel experiments where the only difference is gas atmosphere, the MnO reduction is always faster in CO than in Ar. This result is difficult to explain and not in accordance with



*if two parallel analysis points, the value is an average



*if two parallel analysis points, the value is an average

Figure 5: The concentration of MnO in reacted slag as a function of time for experiments ***a)*** *using coke as substrate* ***b)*** *using charcoal as substrate*

the results of previous studies[12] where the reduction rate of MnO was found to decrease with increasing CO partial pressure. It seems appropriate that this relationship is further investigated using synthetic slags rather that industrial slags. From Figures 4 a and b, it is also apparent that the MnO reduction takes place at a higher rate with charcoal as reductant as compared to industrial coke. This is consistent with earlier findings, supporting the hypothesis[13] that carbon materials with higher CO_2 reactivity and larger active pore area are more effective reductants for MnO (and SiO_2) in slag than less CO_2 reactive materials with less reactive pore area.

In Figure 5, the difference in reduction rate between those slags initially containing metal and those which did not is illustrated. As seen from the figure, the reduction rate is found to be faster when metal is present at the start of the reduction. This may be explained by the larger reaction area provided by the carbon saturated micron sized metal prills in the slag. Another, complementary explanation is the catalytic effect of the metallic iron on the MnO reduction, as outlined in the introduction section.

4. CONCLUSIONS

- A sessile drop technique to kinetically study the reduction behaviour of slags on carbon substrates has been developed and tested. A subsequent technique to mount, section and analyse the reaction products has been employed.
- The EPMA analyses of the reacted slag samples are scattered, assumed mainly due to metallic contents of the starting slag. It is hence proposed that future studies should concentrate on further illuminating the effects of type of reductant and ambient gas atmosphere on the MnO reduction kinetics.
- There are significant differences in the MnO reduction rate with the various parameters:
  - CO gas gives a higher reduction rate than Ar. This is contrary to the expectation that an Ar atmosphere would give a stronger driving force for the reaction MnO+C=Mn+CO
  - Initial metal present increases the reduction rate for all materials used compared to no metal present.
- In general the reduction rate is higher for charcoal than for coke.
- The scattering of the EPMA analyses due to metallic prill content is too big to give valuable information regarding the silica reduction.

5. ACKNOWLEDGEMENTS

The authors wish to acknowledge the project funds provided by the Norwegian Research Council and the Norwegian Ferro-alloy Producers Research Association, through the CarboMat programme.

REFERENCES

[1] Tarby, S. K. and Philbrook, W. O., "The rate and mechanism of the reduction of FeO and MnO from silicate and aluminate slags by carbon–saturated iron" Trans. AIME, 239, 1967, pp.1005-1017.

[2] Daines, W. L. and Pehlke, R. D., "Kinetics of manganese oxide reduction from basic slags by carbon dissolved in liquid iron", Metallurgical Transactions, 2, 1971, pp. 1203-1211.

[3] Pomfret, R. J. and Grieveson, P., "Kinetics of fast initial stage of reduction of MnO from silicate slags by carbon in molten iron", Ironmaking and Steelmaking, No. 5, 1978, pp. 191-197.

[4] Shimoo, T., Ando, S. and Kimura, H., "Rates of MnO reduction from silicate slags with solid carbon", J. Japan Inst. Metals, 48, 1984, No. 9, pp. 922-929.

[5] Upadhya, K., "The kinetics and mechanism(s) of manganese oxide reduction from liquid slag by carbon dissolved in iron", ISS Transactions, 7, 1986, pp. 1-6.

[6] Xu, K., Jiang, G., Ding, W., Gu, L., Guo, S. and Zhao, B., "The kinetics of reduction of MnO in molten slag with carbon saturated liquid iron", ISIJ International, 33,1993, No. 1, pp. 104-108.

[7] Skjervheim T. A., "Kinetics and mechanisms for transfer of manganese and silicon from molten oxide to liquid manganese metal", Dr. Ing. Dissertation, NTH, Trondheim, Norway,1994.

[8] Tangstad, M., "The high-carbon ferromanganese process – coke bed relations", Dr. Ing. Dissertation, NTH, Trondheim, Norway, 1996.

[9] Olsø, V., Tangstad, M, and Olsen, S.E., "Reduction kinetics of MnO-saturated slags", Proc. INFACON 8, The Chinese Society for Metals, Beijing, China,1998, pp. 279-283.

[10] Guo, S. Q., Jiang, G. C., Xu, J. L., Xu, K. D., "Kinetics of reduction of MnO in molten slag with carbon undersaturated liquid iron", J. Iron & Steel Res. Int., 7, 2000, No. 1, pp. 1-5.

[11] Yastreboff, M., Ostrovski, O. and Ganguly, S., "Effect of gas composition on the carbothermic reduction of manganese oxide", ISIJ Int., 43, 2003, No.2, pp.161-165.

[12] Berg, K., Olsen, S. E., "Kinetics and machanism for the carbothermic reductionof MnO and SiO_2 from liquid slags", SINTEF internal report (STF24 A04531), 2004.

[13] Gaal S., Berg K., Tranell G., Olsen S.E., and Tangstad M., "An investigation into aspects of liquid phase reduction of manganese and silica containing slag", 7th International Conference on Molten Slags, Fluxes and Salts, Cape Town, South Africa, Jan. 2004, pp. 651-657.

[14] Safarian, J, Kolbeinsen, L., Gaal, S. and Tranell, G., "The effect of graphite properties on the rate of MnO reduction from high-carbon ferromanganese slag", submitted to INFACON XI, 2007.