

Gaseous Reduction of Mn ores in CO-CO₂ atmosphere

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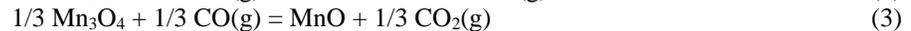
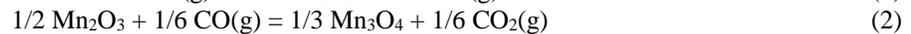
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Abstract – The efficiency in production of manganese ferroalloys is dependent on the gaseous reduction of the higher manganese oxides in the ores used as raw materials. The materials, descending in the furnace, will meet the furnace gas that contains significant amounts of CO(g) and reduce in subsequent steps, the last step being reduction of Mn₃O₄ to MnO. This step may to varying extent occur at temperatures exceeding 800°C, i.e. in the active region of the Boudouard reaction. The gas reduction of Assmang and Comilog manganese ores were investigated in CO-CO₂-atmosphere at temperatures up to 1000°C. It was seen that decreasing ore size correlates to a lower reduction temperature and increasing reduction rate. Similar effect was observed with increasing CO-content in the gas atmosphere. Further, it was found that Comilog ore obtained a complete prereduction at 600°C, whereas reduction of Assmang ore was not complete at 800°C for the majority of the experiments.

1 INTRODUCTION

Manganese ferroalloys are produced in submerged arc furnaces from raw materials such as manganese ore, coke and fluxes. The manganese content in the ores are present as a combination of the potential different oxides, i.e. MnO, Mn₂O₃, Mn₃O₄ and MnO₂. In the industrial furnace, the oxides enter the upper part of the prereduction zone and meet the furnace gas ascending from the melting zone and reduce to MnO in subsequent steps:



Reactions (1)-(3) are exothermic reactions and will hence heat the charge material. The reduction of solid Mn₃O₄ by CO-gas is determined by kinetics rather than thermodynamics. The Boudouard reaction may run simultaneously as the Mn₃O₄-reduction, implying that the CO₂ produced in reaction (3) reacts with solid carbon to form carbon monoxide gas according to reaction (4). Hence, the overall reduction of Mn₃O₄ is given as reaction (5).



Alkalis enter the furnace through the raw materials and may accumulate. Research has shown that alkalis have a catalytic effect on the Boudouard reaction causing it to be of significance at temperatures as low as 800°C[1]. The extent of the Boudouard reaction is an important parameter in terms of the efficiency of the furnace process as the reaction is both carbon consuming and highly endothermic. Thus, ores should have qualities and characteristics that promote a complete gas reduction of Mn₃O₄ prior to entering the active area of the Boudouard reaction. These qualities and characteristics are often noted as ore reactivity or CO-reactivity, which is a function of ore sizing, open pore volume, mineralogy and chemical composition[2]. The extent of the gas reduction of Mn₃O₄ is called the prereduction degree, and according to Tangstad et. al. an industrial prereduction degree of 10% to 40% is typical, but can potentially be as high as 60%[3].

This paper studies the solid state gas reduction behavior of two different manganese ores by varying the CO-content in the gas and sizing of raw materials. Results are discussed in terms of weight behavior as a function of time and temperature.

2 EXPERIMENTAL

2.1 RAW MATERIALS AND EQUIPMENT

The gaseous reduction of two different manganese ores supplied by industry were investigated. Two different raw material sizes for each ore were evaluated and both were analysed. The results can be seen in table 1 where A denotes size fraction -1.36+0.5 mm and B denotes size fraction -4.0+3.33 mm. The composition was determined by X-Ray Fluorescence, except for the MnO₂-content which was determined by titrimetric analysis. All reported Mn that was not MnO₂ was assumed to be MnO and all reported iron was assumed to be Fe₂O₃.

Table 1: Chemical composition of investigated manganese ores. Samples A are in size fraction -1.36+0.5 mm and sample B correlates to size fraction -4.0+3.33 mm

		Comilog A	Comilog B	Assmang A	Assmang B
Mn	TOT	48.4	51.4	46.7	46.5
MnO ₂	%	71.7	76.6	35.5	34.2
Fe	TOT	3.5	2.8	9.6	9.5
SiO ₂	%	5.6	3.5	6.4	6.2
Al ₂ O ₃	%	6.6	5.6	0.5	0.5
CaO	%	0.1	0.1	6.2	6.3
MgO	%	0.2	0.2	1.1	1.1
P	%	0.1	0.1	0.0	0.0
S	%	0.0	0.0	0.1	0.2
TiO ₂	%	0.2	0.1	0.0	0.0
K ₂ O	%	1.1	1.1	0.0	0.0
BaO	%	0.2	0.2	0.5	0.5
CO ₂	%	0.2	0.2	3.1	3.1
Moisture	%	0.4	0.6	0.0	0.0
LOI (950°C)	%	12.8	12.5	4.1	4.0

Table 2 shows the theoretical weight loss correlating to the reactions occurring at temperatures up to 1000°C. The majority of the weight loss in Comilog is due to the reduction of manganese oxides, whereas the reduction of iron oxides accounts for a significant part in Assmang. Further, it can be seen that the ores are dry, where the maximum moisture content is found in Comilog B at 0.6%. The theoretical weight loss from reduction of higher manganese oxides to MnO is 13.9 % and 14.7 % for Comilog A and B, respectively. Corresponding values for Assmang A and B are 6.6% and 6.4%.

Table 2: Calculated weight loss correlating to the different reactions occurring at temperatures up to 1000°C

Reaction	Comilog A Weight loss [%]	Comilog B Weight loss [%]	Assmang A Weight loss [%]	Assmang B Weight loss [%]
$\text{MnO}_2 + \text{CO} = \text{Mn}_2\text{O}_3 + \text{CO}_2$	6.9	7.3	3.3	3.2
$\text{Mn}_2\text{O}_3 + \text{CO} = \text{Mn}_3\text{O}_4 + \text{CO}_2$	2.3	2.4	1.1	1.1
$\text{Mn}_3\text{O}_4 + \text{CO} = \text{MnO} + \text{CO}_2$	4.6	4.9	2.2	2.2
$1/2 \text{Fe}_2\text{O}_3 + 3/2 \text{CO} = \text{Fe} + 3/2 \text{CO}_2$	1.6	1.3	4.2	4.2
CO ₂	0.2	0.2	3.2	3.2
H ₂ O = H ₂ O(g)	0.4	0.6	0.0	0.0
Total	16.0	16.7	14.0	13.9

A thermogravimetric tube furnace was used for the reduction experiments. A schematic of the crucible set up is shown in figure 1(left), where the location of sample, thermocouple and gas inlet and outlet is marked. The sample is located in the lower parts of the crucible and placed on top of a stage/cage in order to ensure an even distribution of gas through the sample. The gas inlet is at the top of the crucible, from where the gas moves through the crucible walls and meets the sample from the bottom. Figure 1(right) shows the crucible, which hangs in a wire that is connected to the mass balance, and its location in the furnace. The furnace is lifted to surround the crucible during heating, while the image shows the furnace before it has been lifted. The furnace measures time, temperature and mass loss at a five second interval. In addition, the gas composition leaving the crucible is measured by a connected gas analyser.

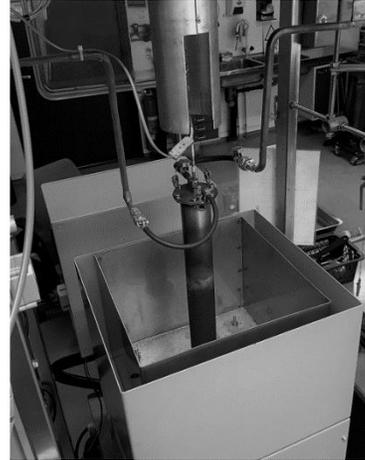
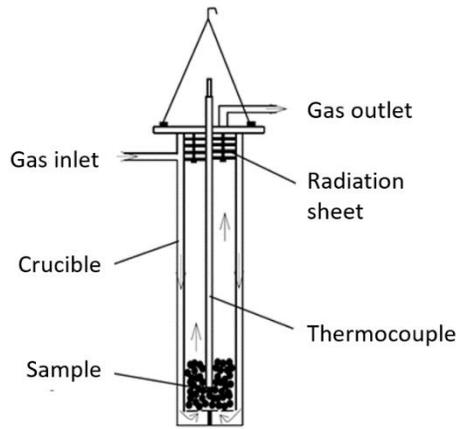


Fig. 1: Picture to the left shows the crucible set up, where location of sample, thermocouple and gas inlet and outlet is marked[4]. Picture to the right shows that the crucible hangs in a wire that is connected to a mass balance, and its location in the furnace, which is lifted to surround the crucible during heating[5]

2.2 PROCEDURE

For each experiment a total of 75 ± 1 g manganese ore were used, where two different size fractions, $-1.36+0.5$ mm and $-4.00+3.33$ mm, have been evaluated. The samples were heated in two different gas compositions (50% CO or 80% CO, where remainder is CO₂) where the total gas flow was 4 l/min. The temperature was increased at a rate of 6 °C/min up to 1000°C. After the crucible reached the target temperature, the furnace was shut down, allowing the crucible to cool down to room temperature in argon gas at 1 l/min for 45 minutes.

The CO-reactivity during the different experiments is determined from the weight loss curves retrieved from the furnace mass log, which directly reflects the reduction rates. In addition to the weight loss obtained from the reduction of manganese oxides, there will be an observed weight loss from the reduction of iron oxides and evaporation of water. It was assumed that iron oxides reduce linearly in temperature range where off-gas analysis confirmed an ongoing reduction. The relation was assumed linear according to furnace temperature, not sample temperature. The amount of moisture in the materials was insignificant and hence not considered.

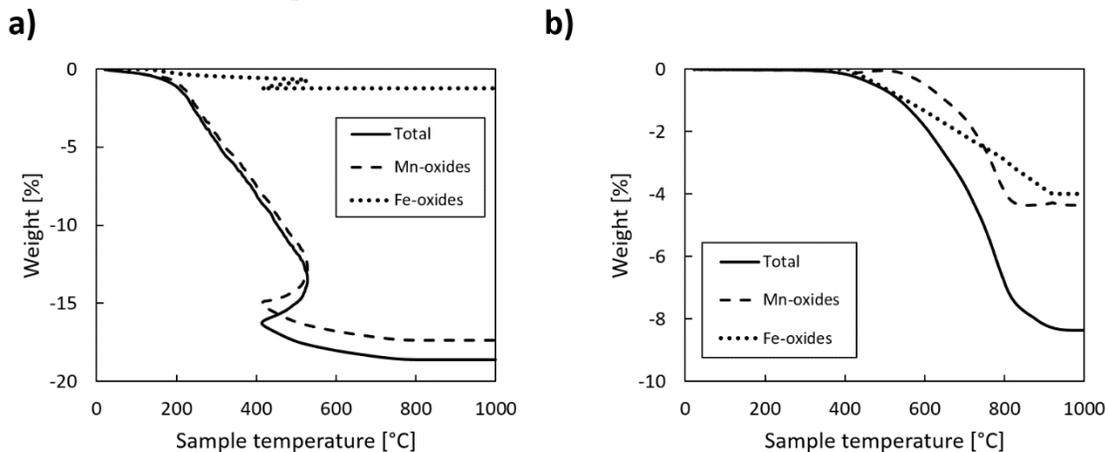


Fig. 2: Weight reduction behaviour for iron oxides, manganese oxides and the respective total weight reduction for Comilog (a) and Assmang (b)

The effect of these assumptions can be seen in figure 2, both for Comilog(a) and Assmang(b), for one of the experiments conducted with sample size A. The effect of weight loss due to reduction of iron oxides can be seen to be insignificant compared to the weight loss accompanying the reduction of manganese oxides in Comilog ore. For Assmang ore, the effect is more significant, however the overall shape of the reduction curves remains unchanged.

3 RESULTS AND DISCUSSION

Figure 3 shows the temperature recording from the thermocouple located at the furnace wall, as well as the temperature recorded by the thermocouple located in the sample for one of the conducted Comilog and Assmang experiments, respectively. The temperature at the furnace wall shows a linear increase corresponding to 6 °C/min according to the heating rate executed for all of the experiments. It can be seen that the initial sample temperatures are lagging somewhat relative to the furnace temperature. At higher temperatures, the sample temperature is affected by the exothermic reactions occurring inside the crucible. This effect is most significant for Comilog charges due to the high oxygen level, as is observed by the peak at approximately 40 minutes process time. The sample temperatures for Assmang are relatively close to the furnace wall temperature throughout the whole experiment.

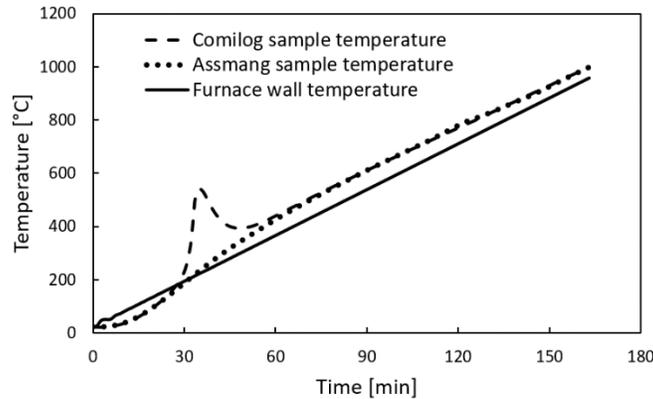


Fig. 3: Furnace temperature and sample temperatures for Comilog and Assmang charge, respectively

Figure 4 shows the relative weight as a function of process time and sample temperature for experiments conducted with Comilog ore. The end temperature for all conducted experiments was 1000°C, reached after approximately 165 minutes, however the weight vs time figure includes values up to 100 minutes process time, correlating to approximately 670°C, in order to better illustrate the difference between the charges at lower temperatures. The weight loss remained nearly constant at higher temperatures, as confirmed by figure 4b.

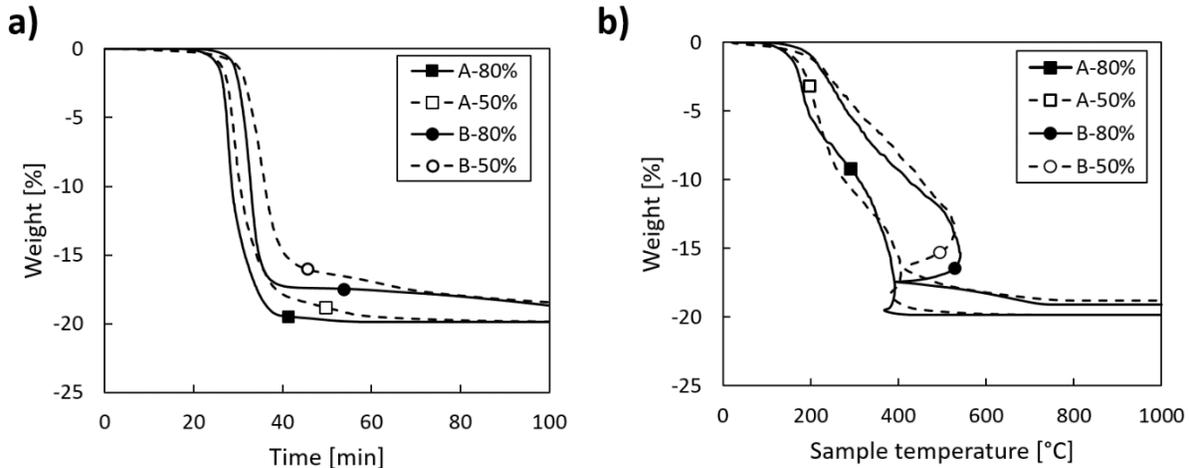


Fig. 4: Weight reduction for Comilog experiments as a function of time (a) and sample temperature (n) as recorded by the furnace mass log

At approximately 20-30 minutes process time, i.e. 200°C, the reduction rate increases and the charges have obtained a complete prereduction within 10 minutes process time. The sample temperature deviates from the furnace wall temperature, as the temperature inside the crucible is affected by the heat released by the exothermic reactions. This effect is observed in the common “Z-shape” of the curves, which is normally observed for ores containing MnO₂. Further, it is seen that smaller particle size increases the reduction rate. Hence, the rapid reduction stage is initiated at a lower temperature. The effect of varying CO-content in the gas atmosphere on the reduction rate is observed to a

smaller extent than varying raw material size. Nonetheless, it can be seen that increasing content of CO(g) results in a lower initiation temperature for the offset of the rapid reduction stage, as well as an increase in the reduction rate.

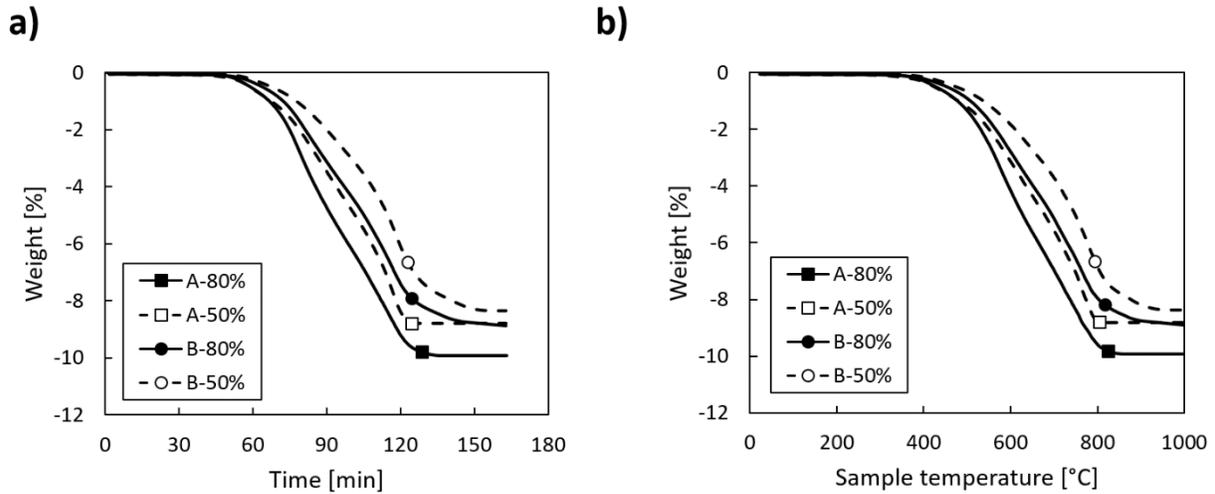


Fig. 5: Weight reduction for Assmang charges as a function of time (a) and sample temperature (b) as recorded by the furnace mass log

Figure 5 shows the weight as a function of process time and sample temperature for experiments conducted with Assmang ore. The effect of raw material size is observed, where a smaller size results in an initiation of reduction at a lower temperature compared to larger raw material size. The increasing CO-content appears to have a smaller effect on the reduction rates compared to material size, in accordance with the reduction behavior of Comilog. It can be seen that the majority of the Assmang charges have not reached a complete prerreduction at 800°C. This implies that Assmang ores will reduce in the active region of the Boudouard reaction, which has been seen to be significant at temperatures exceeding 800°C. Thus, Assmang ore results in an increasing energy and carbon consumption compared to Comilog ore.

Figure 6 shows the reduction rates for Comilog experiments and Assmang experiments in a) and b), respectively. The rates were found by evaluating the change in relative weight (%) per minute process time. When not considering the rapid reduction stage for Comilog, the rates were highly similar at all process times and temperatures. As such, the figure is focused at the range of these rapid reduction stages. The rates start to increase at approximately 25 minutes process time for the smaller material size, whereas the increase is observed at 30 minutes process time for the larger size. Further, it can be seen that experiments run with 80% CO obtains a higher maximum reduction rate compared to experiments conducted with 50% CO. As for Assmang, it can be seen that the behaviour of the reduction rates are quite similar for the different experiments. At approximately 50 minutes process time, it is seen that the reduction rates start to increase up to common peak point at 120 minutes process time, i.e. c. 800°. Comparison of the reduction rates for Assmang and Comilog shows that Comilog reduces at a considerable lower temperature, in addition to obtaining a significantly higher rate. The rates differ with a factor of 18 for the experiments that showed the highest rate for the two respective ores.

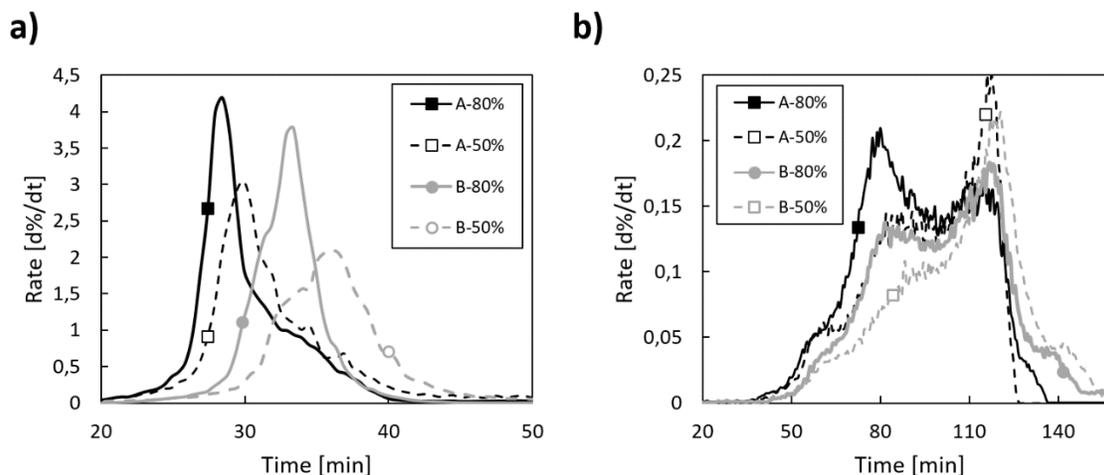


Fig. 6: Reduction rates (d%/dt) for Comilog charges (a) and Assmang charges (b). The rates were found by evaluating the change in relative weight reduction (%) per minute process time

4 CONCLUSIONS

The gaseous reduction behaviour of Assmang and Comilog manganese ores were investigated in CO-CO₂ atmosphere at temperatures up 1000°C. Two different raw material sizes (-1.35+0.5 mm and -4.0+3.33 mm) and two different gas atmospheres (80%CO and 50% CO, with remainder CO₂) were evaluated. It was found that decreasing raw material size correlates to a lower reduction temperature and an increasing reduction rate. Further, it was seen that experiments run with 80% CO obtained a higher maximum reduction rate compared to experiments run with 50% CO. The effect of raw material size was observed to a greater extent than increasing amount of CO. Comilog ore had obtained a complete prereduction at temperatures lower than 600°C, whereas the majority of the Assmang experiments were not complete at 800°C.

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REFERENCES

- [1] Ishak, R., *Reaction kinetics for reduction of manganese ore with carbon monoxide in the presence of carbon*, in *Dr. Ing Thesis*. 2002, Norwegian University of Science and Technology, Trondheim: Department of Materials Science and Engineering.
- [2] Olsen, S.E., M. Tangstad, and T. Lindstad, *Production of Manganese Ferroalloys*. 2007: Tapir Academic Press.
- [3] Ishak, R. and M. Tangstad, *Degree of prereduction without coke consumption in industrial furnaces*. INFACON XI, 2007: p. 268-279.
- [4] Tangstad, M., *Summary of prereduction experiments in the Disvadri furnaces with industrial materials in Gasferrosil v.2*. SINTEF Materials and Chemistry, 2017.
- [5] Turkova, K., D. Slizovskiy, and M. Tangstad, *CO reactivity and porosity of manganese materials*. ISIJ international, 2014. **54**(6): p. 1204-1208.