1. Introduction

Carbothermal reduction of pure MnO to manganese carbide Mn₇C₃ by reaction (1) under standard conditions \((P_{CO} = 1 \text{ atm})\) starts at 1340°C (calculated using the standard Gibbs free energies from Ref. 1))

\[
7\text{MnO} + 10\text{C} = \text{Mn}_7\text{C}_3 + 7\text{CO},
\]

\[
\log K = -93 \frac{807}{T} + 58.24
\] .................(1)

In industrial production of manganese alloys, manganese oxide is reduced from molten slag. When the MnO content in the slag decreases below saturation level, the reduction is slow and incomplete. Manganese ores start to melt at relatively low temperatures, below 1200°C (depending on the ore chemical composition, see Ref. 2)); carbothermal reduction at a temperature of 1200°C is possible at decreased CO partial pressure; equilibrium CO partial pressure for reaction (1) at this temperature is 0.167 atm. Reduction/prereduction of manganese ore in the solid state can be a significant step towards improving overall efficiency of production of manganese alloys.

Reduction of manganese ore in the solid state was studied in works.\(^3\)–\(^6\) Carbothermal reduction of oxides in manganese ore includes a number of stages. At the first stage, higher manganese oxides MnO₂, Mn₂O₃ and Mn₃O₄ are reduced to MnO and iron oxides to FeO. These reactions proceed through the gas phase; oxides are reduced by carbon monoxide with formation of carbon dioxide, which is converted to CO by the Boudouard reaction.

This stage is fast; it takes 6–10 min, is independent of temperature and slightly depends on ore particle size.\(^7\) An apparent activation energy of reduction reaction at this stage calculated by Misra\(^4\) was 37.4 kJ/mol, while the activation energy found by Eric and Burucu\(^7\) was 61 kJ/mol. Most researchers consider that reaction rate is mix-controlled by chemical reaction (intrinsic control) and carbon monoxide mass transfer.

The second stage is generally described as metal phase development which begins with iron nucleation, followed by Fe–Mn carbide and silicate formation. At this stage, three major phases were identified: manganese–iron carbide, MnO and the slag phase. Several reduction reactions were proposed for this stage in Ref. 7):

(1) Gas–solid MnO reduction by CO:

\[
\text{MnO(s)} + \text{CO(g)} \rightarrow \text{(Mn, Fe)C}_x + \text{CO}_2
\] .................(2)

C + \text{CO}_2 \rightarrow 2\text{CO}

(3)

This reduction reaction proceeds at temperatures above 1200°C and was shown to be affected by temperature and by changing the gas atmosphere from argon to CO.\(^7\)\(^8\) Chemical reaction between oxide phase and reducing gas was suggested to control this stage with the apparent activation energy 153.3 kJ/mol.\(^7\)

(2) Reduction by carbon in manganese–iron carbide:

\[
\text{MnO(s)} + \text{C(carbide)} = \text{Mn(carbide)} + \text{CO(g)}
\] .........(4)

This reaction comes into effect when the formed metal-
lic/carbide phase has mostly covered the oxide phase hindering the gas–solid oxide reduction reaction. Gaseous product CO escapes through the pores and micro-cracks in the carbide phase created by the pressure generated by the gas.\textsuperscript{7} The reduction rate in this case is low and is limited by diffusion of Mn\textsuperscript{2+} ions in the oxide phase. The activation energy for this reduction process was found to be 310.4 kJ/mol.

(3) At the final stage, manganese oxide dissolved in the silicate phase was reduced by carbon in the carbide phase:

\[
\text{MnO(silicate)} + \text{C(carbide)} = \text{Mn(carbide)} + \text{CO(g)} \ldots (5)
\]

The silicate phase is formed as a result of the reaction between SiO\textsubscript{2}, CaO, MnO and some impurities.

The effect of gas atmosphere on the carbothermal reduction of manganese ores has been studied mostly in CO, argon or in CO–Ar atmospheres. Authors of works\textsuperscript{3,5,7–12} concluded that lowering CO partial pressure increases both the rate and extent of reduction. The fastest rate of carbothermal manganese ore reduction was achieved in inert atmosphere. Different results were obtained by J. Safarian,\textsuperscript{13} who observed a higher rate of reduction of MnO from molten silicate by graphite substrate at 1 600°C in CO gas than in argon. At 1 600°C, MnO can be reduced to the metallic/carbide phase by CO, which is not feasible for reduction of MnO from the ore in the solid state.

Effect of particle size on reduction of Wessels ore was studied by Akdogan and Eric\textsuperscript{3,12} under argon at 1 300°C. They revealed that the first rapid stage of reduction was not affected by ore particle size while the rate of the second reduction decreased with increased ore particles size. They also found that graphite particle size increase in the range 150 to 210 \(\mu\)m resulted in significant decrease in the reduction rate. Similar effect of the particle size on the ore reduction was observed in works\textsuperscript{7,9,14}

This paper studied solid state carbothermal reduction of Groote Eylandt (Australian) and Wessels (South African) manganese ores in different gas atmospheres with the aim to establish the reduction rate and mechanisms and conditions for solid state reduction. Reduction of pure manganese oxide MnO in different gas atmospheres was presented in work\textsuperscript{15}

2. Experimental

The manganese ores examined in this paper were Groote Eylandt ore from Australia, and Wessels ore from South Africa. Two grades of Groote Eylandt ore were studied: GE-PF ore with low silica contents and GE-PS ore with high silica content. Characterisation of manganese ores was presented in work\textsuperscript{21}. Their compositions are given in Table 1.

The ores were grounded into different particle size fractions. The size fraction used in majority of manganese ore reduction experiments was –45 + 150 mm. All manganese ores were preheated in air at 1 000°C for 3 h before the reduction. The XRD analysis of preheated ores showed that the main phases were Mn\textsubscript{4}O\textsubscript{3} and Mn\textsubscript{3}O\textsubscript{4} for Wessels and GE-PF ores and Mn\textsubscript{2}O\textsubscript{3}, Mn\textsubscript{3}O\textsubscript{4} and SiO\textsubscript{2} for GE-PS ore (see work\textsuperscript{22}).

Synthetic graphite powder <20 \(\mu\)m was mechanically mixed with manganese ores powder in different proportions.

The gases used in these experiments were high purity argon, ultra high purity hydrogen, high purity helium, and carbon monoxide which were all supplied by Linde (Fairfield, Australia). The gases were passed through traps filled with Drierite and a 4A molecular sieve for purification and removal of moisture.

Composition of the gas introduced into the reactor was controlled by mass flow controllers. Four mass flow controllers (5850E Brooks Instruments) regulated the gas flow rates of argon, hydrogen, helium and carbon monoxide.

Experiments were conducted in a vertical tube furnace with Kanthal Super 1800-MoSi\textsubscript{2} resistance-heating elements. A schematic of the experimental set up is presented elsewhere.\textsuperscript{15} The off-gas in isothermal experiments was analysed on-line using a CO–CO\textsubscript{2} infrared analyser “Advance Optima” supplied by Hartmann & Braun (Austria). The instrument was calibrated using standard gas mixtures. The analyser was connected to the reactor off-gas outlet through a series of filters to reduce contamination of the infrared sensors.

The H\textsubscript{2}O content was measured using a dew point monitor General Eastern Hygro M4/D-2, manufactured by General Eastern (Woburn, USA). The detecting range of the dew point monitor was –35°C to +25°C at ambient temperature of 25°C with an accuracy of 0.2°C.

A 1 g mixture of manganese ore with graphite with known proportion was placed in a graphite crucible. Then the total weight was measured and a sample was introduced to the reactor, which was sealed and flushed with working gas at room temperature for 10 min before it was moved down to the hot zone from the top of the furnace. The time was noted when the reactor was placed into the hot zone of the furnace.

The temperature inside the reactor was monitored by a Type-B thermocouple placed just above the crucible. The total flow rate of the gas was kept at 1.2 l/min in all experiments.

After reaction, the reactor was removed from the furnace to quench the sample. When the reactor had cooled to room temperature, the crucible was extracted and the total weight was taken again to measure the weight loss of the sample. The reduced sample was taken from the crucible and prepared for further analysis by XRD, optical microscopy,

| Table 1. Composition of manganese ores (mass%). |
|---------------------------------------------|
| Ore          | Mn  | Fe  | SiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | P\textsubscript{2}O\textsubscript{5} | CaO   | K\textsubscript{2}O | MgO  | Mn/Fe |
|--------------|-----|-----|---------------------|-----------------------------|-----------------------------|-------|-------------|------|-------|
| Wessels      | 49.2| 10.2| 3.79                | 1.37                        | 0.08                        | 7.57  | -           | 0.66 | 4.85  |
| Groote Eylandt GE-PF | 55.5| 3.94| 5.32                | 3.41                        | 0.202                       | 0.157 | 1.34        | 0.15 | 14.1  |
| Groote Eylandt GE-PS | 38.9| 4.61| 34.4                | 3.27                        | 0.16                        | 0.106 | 0.505       | 0.08 | 8.44  |

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SEM, EPMA and LECO analyses.

3. Results

3.1. Non-isothermal Reduction

Temperature-programmed carbothermal reduction experiments were carried out in helium and hydrogen in the temperature range 300–1500°C with the ramping rate of 5°C/min. Figures 1–6 illustrate the evolution of gaseous products and sequence of transformations in the non-isothermal reduction of Wessels, GE-PF and GE-PS ores.

Evolution of gaseous products together with XRD and XRF analyses revealed several stages of carbothermal reduction of manganese ores.

The reduction of Wessels manganese ores in helium (Fig. 1) started with reduction of Mn₂O₃ to Mn₃O₄ and Fe₂O₃ to FeO at 550–600°C with evolution of CO₂ (reactions (6) and (7)):

\[ 3\text{Mn}_2\text{O}_3 + \frac{1}{2} \text{C} \rightarrow 2\text{Mn}_3\text{O}_4 + \frac{1}{2} \text{CO}_2 \] \hspace{1cm} (6)

\[ \text{Fe}_2\text{O}_3 + \text{C} \rightarrow 2\text{FeO} + \frac{1}{2} \text{CO}_2 \] \hspace{1cm} (7)

Fig. 1. Non-isothermal carbothermal reduction of Wessels ore in helium. Ramp rate 5°C/min.

Fig. 2. Non-isothermal carbothermal reduction of Wessels ore in hydrogen. Ramp rate 5°C/min.

Fig. 3. Non-isothermal reduction of GE-PF ore with 23 mass% of graphite in helium. Ramp rate 5°C/min.

Fig. 4. Non-isothermal reduction of GE-PF ore with 23 mass% of graphite in hydrogen. Ramp rate 5°C/min.

Fig. 5. Non-isothermal reduction of GE-PS ore in helium. Ramp rate 5°C/min.

Fig. 6. Non-isothermal reduction of GE-PS ore in hydrogen. Ramp rate 5°C/min.
At temperatures above 900°C, carbon monoxide was evolved and at temperatures above 950°C carbon dioxide became undetectable. Evolution of CO$_2$ and its replacement by CO is determined by the Boudouard reaction (3) of carbon gasification.

Further reduction proceeded with conversion of Mn$_3$O$_4$ to MnO and “FeO” to metallic iron or iron carbide by reactions (8) and (9).

$$\text{Mn}_3\text{O}_4 + (x+y)\text{C} \rightarrow 3\text{MnO} + x\text{CO}_2 + y\text{CO} \quad \ldots \ldots \ldots (8)$$

“FeO”$ + \text{C} \rightarrow (\text{Fe}, \text{C}) + \text{CO} \quad \ldots \ldots \ldots (9)$$

Overlapping of reduction stages in non-isothermal experiments does not allow determining accurately the degree of reduction at different stages. On the basis of chemical composition, this reduction stage is estimated to extend to 45% of reduction for Wessels ore, 38% for GE-PF ore and 40% for GE-PS ore. Upon the completion of this stage the only remaining manganese oxide was MnO.

Conversion of MnO to manganese (ferromanganese) carbide started at temperatures around 1 050°C which is lower than for pure manganese oxide MnO (see work$^{[15]}$).

Gas evolution and reduction curves obtained in the carbothermal reduction of Wessels ore in hydrogen are presented in Fig. 2. Analysis of the off-gas composition revealed the three major stages.

The first stage comprised the series of consecutive steps of reduction of higher manganese oxides to MnO and iron oxides to metallic iron by hydrogen with water evolution. The overall reduction reactions at this stage are

$$\text{Mn}_3\text{O}_4 + \text{H}_2 \rightarrow 2\text{MnO} + \text{H}_2\text{O} \quad \ldots \ldots \ldots (10)$$

$$\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O} \quad \ldots \ldots \ldots (11)$$

These reactions started at low temperature of $<$300°C and were completed at around 950°C when water vapour became undetectable. At the second stage, manganese oxide MnO was reduced by carbon to manganese (ferromanganese) carbide by reaction (12).

$$\text{MnO} + \text{C} \rightarrow (\text{Fe}, \text{Mn}) \text{ carbide} + \text{CO} \quad \ldots \ldots \ldots (12)$$

The maximum rate of reduction was manifested by the major peak in carbon monoxide evolution at about 1 180°C. At temperatures above 1 300°C, silica was partly reduced, presumably from the semi-molten slag.

Major stages in the reduction of Groote Eylandt ores were the same as of Wessels ore. Although, reduction of MnO from the molten slag played a more significant role, particularly, in the reduction of high-silica GE-PS ore.

Gas evolution and reduction curves obtained in reduction of GE-PF ore in helium and hydrogen are shown in Figs. 3 and 4 correspondingly. In both helium and hydrogen atmospheres, reduction began with the formation of MnO and Mn$_2$O$_3$ to Mn$_3$O$_4$ and higher iron oxides to “FeO” started at about 400°C. In the second reduction stage, Mn$_3$O$_4$ was reduced to MnO and iron oxides to metallic iron. These two stages were indistinguishable and combined into one in reduction in hydrogen, which began at 300°C.

Higher manganese and iron oxides were reduced in a helium atmosphere by carbon with formation of CO$_2$ at temperatures below about 1 000°C; at higher temperatures, CO evolved. This reflects thermodynamics and kinetics of the Boudouard reaction. The CO$_2$ evolution curve had a major peak at 920°C, which was closely followed by the CO peak at about 950°C. These peaks are of the same origin and are distinguished only as a result of changing conditions for the Boudouard reaction.

Conversion of manganese oxides to MnO and iron oxides to metallic iron at temperatures above about 1 000°C overlapped with reduction of MnO to ferro-manganese carbide. This process slowed down at about 1 180°C, when molten slag started to form. The rate of MnO reduction from molten slag peaked up at 1 400°C. The final extent of reduction was above 100% indicating reduction of silica from the molten slag at high temperatures.

In reduction experiments in hydrogen (Fig. 6), higher manganese oxides were reduced to MnO and iron oxides to Fe by hydrogen at temperatures below 900°C with the formation of water vapour; at higher temperatures, reduction was predominantly proceeded by carbon. The rate of this stage in hydrogen was faster than in helium and completed at around 1 150°C before the slag started to form.

### 3.2. Isothermal Reduction

Temperature interval for reduction of Wessels and Groote Eylandt ores in the solid state is quite limited. Temperatures of beginning of melting of different ores were established in work$^{[3]}$ by microscopic examination of samples heated in helium to different temperatures. Wessels ore was solid at temperatures up to 1 250°C and GE-PF ore up to 1 200°C;
GE-PS ore started to melt at about 1100°C. This defines the temperature limit of 1200°C; at temperatures below 1100°C, the reduction of manganese ores is slow. Therefore, isothermal reduction experiments were conducted at 1100 and 1200°C. Reduction curves for Wessels and Groote Eylandt ores obtained at these temperatures in different gas atmospheres are compared in Fig. 7 (1100°C) and Fig. 8 (1200°C). They show that reduction rate increased with increasing temperature and reduction was the fastest in hydrogen.

Effects of temperature and gas atmosphere on the reduction of GE-PF, GE-PS and Wessels ores can be summarised as follows:

- Rate and degree of reduction of manganese ores increased with increasing temperature from 1100°C to 1200°C;
- Reduction was faster in helium than in argon (the difference was insignificant in reduction of GE-PS ore at 1200°C), and much faster in hydrogen than in helium;
- In the process of carbothermal reduction of ores in hydrogen at 1200°C, silica was reduced.
- Reduction of both GE ores in hydrogen was faster than of MnO, particularly at 1100°C.
- Reduction of both GE ores was slower than of Wessels ore; the first stage of reduction of GE-PF in hydrogen was close to that of Wessels ore.

### 3.3. Effect of Carbon Content

The effect of carbon content on carbothermal reduction of manganese ores was studied in hydrogen at 1200°C by changing graphite content in the mixture with the ore in the range 5–30 mass%. The effect of carbon content on extent and rate of manganese ores reduction is shown in Figs. 9–11.
The first reduction stage included reduction of higher manganese oxides to MnO and iron oxides to metallic iron by hydrogen and was not affected by the carbon content in the graphite–ore mixture.

Within the range 12–30 mass% carbon content in the mixture had a minor effect on the extent of reduction of Wessels ore, however, affected the rate of the second reduction stage (Fig. 9). Increasing the graphite content from 12 to 20 mass% in the mixture with GE-PF ore increased the reduction rate and final extent of reduction. Carbon content in the range 20–30 mass% did not affect the reduction rate; the final extent of reduction was close to 100% (Fig. 10).

In the case of GE-PS ore, increasing carbon content up to 24 mass% increased the rate and extent of reduction and had no effect in the range 24–30 mass%.

Carbon content strongly affected the final phase composition of reduced manganese ore, which is given in Table 2. When carbon content in the graphite–Wessels ore mixture was 12–16 mass%, manganese oxide was reduced to metallic α-Mn and ferromanganese carbide (Mn, Fe)$_2$C$_6$. In the sample reduced with 18 mass% carbon, only carbide (Mn, Fe)$_2$C$_6$ was observed. When carbon content increased to 20 mass% and above, (Mn, Fe)$_7$C$_3$ was formed.

Reduction of GE-PF ore with 12–14.5 mass% carbon was incomplete; major phases in the reduced sample were tephroite (Mn$_2$SiO$_4$) and low carbon iron–manganese carbide Mn$_2$C$_6$. Unreduced MnO was also detected. Samples reduced with 15–16 mass% carbon contained high carbon manganese carbide (Mn, Fe)$_2$C$_3$ and tephroite. With addition of carbon above 20 mass% the final product contained manganese (ferromanganese) silico-carbide Mn$_5$SiC and (Mn, Fe)$_7$C$_3$. Oxides were not detected by XRD.

Manganese silicates were not detected in the GE-PS ore samples reduced with graphite content of 14 mass% and above, although complete MnO reduction (from silicate) was approached only when samples contained 24 mass% C. Two silicon-carbide phases were identified in samples produced with 11–20 mass% C, (Mn, Fe)$_{22.6}$Si$_{5.4}$C$_4$, and (Mn, Fe)$_5$SiC. In samples with 25–30 mass% C, manganese silicide (Mn, Fe)$_5$Si$_1$ was also observed.

| Carbon, wt% | Wessels ore | GE-PF ore | GE-PS ore |
|------------|------------|-----------|-----------|
| 5–10       | (Mn,Fe), Mn$_2$C$_6$, MnO | (Mn,Fe), (Mn,Fe)$_2$C$_6$, MnO | Mn$_2$SiO$_4$ |
| 11         | (Mn,Fe), Mn$_2$C$_6$ | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$, MnO | Mn$_2$SiO$_4$, Mn$_2$SiO$_4$, MnO |
| 12         | (Mn,Fe), Mn$_2$C$_6$ | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$, MnO | Mn$_2$SiO$_4$, Mn$_2$SiO$_4$, MnO |
| 13         | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$ | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$, MnO | Mn$_2$SiO$_4$, Mn$_2$SiO$_4$, MnO |
| 14         | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$ | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$, MnO | Mn$_2$SiO$_4$, Mn$_2$SiO$_4$, MnO |
| 15         | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$ | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$, MnO | Mn$_2$SiO$_4$, Mn$_2$SiO$_4$, MnO |
| 16         | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$ | (Mn,Fe)$_2$C$_6$, Mn$_2$SiO$_4$, MnO | Mn$_2$SiO$_4$, Mn$_2$SiO$_4$, MnO |
| 17         | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |
| 18         | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |
| 19         | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |
| 20         | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |
| 21         | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |
| 22         | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |
| 23         | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |
| 24         | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |
| 25         | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |
| >25        | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC | (Mn,Fe)$_2$C$_6$, (Mn,Fe)$_5$SiC |

3.4. Effect of Particle Size

Effect of the ore particle size on carbothermal reduction of manganese ores at 1 200°C in hydrogen is shown in Figs. 12–14. No visible effect on the first stage of reduction was observed for the Wessels (Fig. 12) and GE-PF (Fig. 13).
ores. The first stage of reduction of GE-PS ore (Fig. 14) with a particle size in the range 300–850 μm was slower than the rate of reduction of the ore in the size range <45–250 μm; however, within these ranges, the particle size had no effect. The second stage of reduction of all ores was strongly affected by the ore particle size. The reduction rate increased with decreasing ore particle size.

4. Discussion

Effect of temperature on the rate of carbothermal reduction of manganese ores agrees with literature data; the reduction rate increases with increasing temperature.

Carbothermal reduction of Wessels ore in argon was studied by Eric and Burucu by TGA 7); the degree of reduction rate increased with increasing temperature. The MnO carbothermal reduction was fastest in hydrogen, and was faster in helium than in argon. The strong effect of gas atmosphere on the rate of manganese oxides reduction indicates that external and internal mass transfer of gaseous species involved in the reaction play an important role in the reduction kinetics. The difference between Ar and He is the degree of resistance that they impose onto the diffusivity of other gaseous species. Diffusivity of CO in helium and argon, calculated using the Chapman–Enskog formula 22 at 1 400°C and 1 atmosphere is 16.9 cm² s⁻¹ and 3.6 cm² s⁻¹ respectively. The difference is a factor of 4.7.

Diffusivity of CO in hydrogen and helium is about the same, therefore internal and external mass transfer is not a factor distinguishing carbothermal reduction of manganese oxides in hydrogen and helium. However, hydrogen is involved in the reduction process. Hydrogen reduces higher manganese oxides to MnO and iron oxides to metallic iron in the first reduction stage. Reacting with carbon it forms methane (reaction (14)) which can reduce MnO to Mn₇C₃ by reaction (15):

\[ C + 2H_2 \rightarrow CH_4 \]  \hspace{1cm} (14)

\[ 7\text{MnO} + 10\text{CH}_4 = \text{Mn}_7\text{C}_3 + 20\text{H}_2 + 7\text{CO} \] \hspace{1cm} (15)

Although partial pressure of methane in the gas phase is low (0.01–0.03 atm in the range of experimental temperatures), the carbon activity of the gas phase in equilibrium with graphite is 1.0, which is sufficient for manganese carbide formation. In general, solid–gas reactions are faster than solid–solid reactions. Methane may act as a means for carbon transportation, which accelerates the overall reduction process.

Partial pressure of methane as a function of temperature calculated for \( P_{\text{H}_2} = 1 \text{ atm} \) is presented in Fig. 15. This figure also presents partial pressure of CO₂ in equilibrium with graphite and MnO. At temperatures below 1 300°C, partial pressure of methane is significantly higher than partial pressure of CO₂ (about 2 orders in magnitude at 1 200°C). Therefore, following analysis in Ref. 18, methane mass transfer from carbon to MnO is expected to
be much faster than CO\textsubscript{2} mass transfer from MnO to graphite. The chemical reaction with intermediate methane is also expected to be faster than with CO\textsubscript{2} as it depends on the partial pressure of a reactant.

Manganese oxides in Wessels ore were reduced in the solid state. Formation of a liquid phase in the process of reduction of Groote Eylandt ores was a significant factor affecting the ore reduction. In reduction of GE-PF ore by methane containing gas studied by Anacleto et al.,\textsuperscript{20} extent and rate of reduction significantly decreased with increasing temperature from 1 100°C to 1 200°C; degree of reduction of this ore at 1 200°C was slightly above 50% after 5 h of reaction. This was attributed to the formation of a liquid phase and decrease in the interfacial reaction area with blockage of methane-hydrogen gas access to the ore interior. Doping of the GE-PF ore with lime (10–15% CaO) increased the ore melting temperature and significantly enhanced reduction rate and extent at 1 200°C.\textsuperscript{29}

Carbothermal reduction behaviour of GE ores was very different from that observed in reduction by methane-containing gas. The major difference between these processes is obvious: carbon is intimately mixed with oxides in the carbothermal reduction, while in reduction by CH\textsubscript{4}-H\textsubscript{2} gas, carbon is delivered to the ore interior from the gas phase. This process includes methane adsorption, which depends strongly on the available surface sites.

High iron oxide and low silica concentrations in Wessels ore can be major factors explaining its superior reduction properties. Total (Mn+Fe) concentration in GE-PF and Wessels ores is about the same—near 60%. 38–45% of reduction of these ores in hydrogen (conversion of higher manganese oxides to MnO and iron oxides to metallic iron) was achieved in the same time—5–7 min of reduction.

In further reduction of Wessels and GE-PF ores, manganese oxide was predominantly reduced from the solid MnO phase; only at the later stage of reduction of GE-PF ore MnO was reduced from the manganese silicate. While MnO reduction from Wessels ore in hydrogen proceeded at high rates, its reduction from GE-PF ore slowed down after the first reduction stage significantly.

The metallic iron formed in the first reduction stage provided nuclei for further growth of metallic phase\textsuperscript{5,12,21}; this can be a major factor explaining significant difference in the rate of reduction of MnO oxide to ferromanganese carbide from Wessels ore, in which iron content was 10.2 mass\%, Groote Eylandt ores (3.9 wt\% in GE-PF and 4.6 mass\% in GE-PS).

Effects of carbon content and ore particle size on carbothermal reduction of MnO and manganese ores reported in literature\textsuperscript{5,7,12,18} are in agreement with findings of this work.

5. Conclusions

Solid state reduction of Wessels ore proceeds in hydrogen at a high rate at 1 200°C. The reduction temperature of Groote Eylandt GE-PS ore is limited by a temperature of 1 100°C. Although degree of reduction of both GE-PF and GE-PS ores in hydrogen achieved 90–95\%, the reduction is slow; in practical sense only pre-reduction of GE ores is feasible in the solid state.

The manganese ore chemistry had a significant effect on the ore melting temperature, reduction behaviour and phase composition of a reduced sample.

Carbothermal reduction of manganese ores proceeded in two main stages. In the first stage high manganese oxides were reduced to MnO and iron oxides to metallic iron. The second stage involved reduction of manganese oxides to ferromanganese carbide.

Increasing temperature in the range 1 100°C to 1 200°C increased the reduction rate and degree. The reduction was faster in hydrogen than in helium, and faster in helium than in argon, although for GE-PS ore at 1 200°C the difference in the reduction rate in argon and helium was insignificant. Silicon was reduced at 1 200°C in carbothermal reduction of ores in hydrogen. Wessels ore reduction rate was faster than both GE ores.

Faster reduction of manganese ores in hydrogen than in inert gases was explained by formation of methane which was involved in the reduction process.

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