REDUCTION OF MANGANESE ORES BY METHANE-CONTAINING GAS

O. Ostrovski[1], N. Anacleto[1] and S. Ganguly[2]

[1]School of Materials Science and Engineering, University of New South Wales, Sydney, 2052 Australia.
E-mail: o.ostrovski@unsw.edu.au
[2]Tasmanian Electrometallurgical Company, Bell Bay, Tasmania 7253, Australia.
E-mail: Samir.Ganguly@BHPBilliton.com

ABSTRACT

Reduction of Groote Eylandt (Australia) and Wessels (South Africa) manganese ores using CH_4*-*H_2*-Ar gas mixture was investigated in a fixed bed laboratory reactor in the temperature range 1000–1200°C. The extent and kinetics of manganese ore reduction as a function of gas composition and temperature were determined by on-line off-gas analysis using mass-spectrometer and dew point sensor. Morphology of ores and its change in the course of reduction was examined by optical and scanning electron microscopy. Phases of raw materials and reduced samples were analysed by XRD and EPMA.*

Manganese oxides were reduced to carbide Mn_7C_3*. High extent and rate of reduction by methane-containing gas in comparison with carbothermal reduction were attributed to high carbon activity in the reducing gas, which was in the range 15 - 50 (relative to graphite). The reduction rate of Wessels manganese ore increased with increasing temperature. Reduction rate and extent of Groote Eylandt manganese ore achieved maximum at 1050°C. The decrease in rate and extent of reduction of Groote Eylandt ore at higher temperatures, particularly at 1150-1200°C, was due to sintering and formation of semi-liquid silicate slag. The optimum conditions for the reduction of manganese ores were established as follows: a) temperature: 1150-1200°C for Wessels and 1050-1100°C for Groote Eylandt ores, b) methane concentration: 10-15 vol%, c) hydrogen concentration: above 30 vol%, (d) size: 1-3 mm. An addition of lime (10-15 wt% CaO) to the Groote Eylandt manganese ore increased melting temperature of slag and significantly increased the rate and extent of reduction at elevated temperatures.*

1. INTRODUCTION

In production of manganese alloys in electric or blast furnaces, MnO is reduced from molten slag by carbon to manganese (ferromanganese) carbide. Decrease in the concentration of manganese oxides in slag below the saturation level slows down the reduction [1] that limits the extent of reduction and results in production of high-manganese slag. Reduction of manganese ore in the solid state by solid carbon, hydrogen or carbon monoxide does not go beyond MnO. This is seen from the Mn-O-C stability diagram in Fig. 1. At temperatures when manganese ore is solid, low oxygen partial pressure needed for reduction of MnO to metallic manganese or manganese carbides cannot be achieved (in practical sense) using solid carbon, hydrogen or carbon monoxide.

However, it can be achieved using methane-hydrogen gas mixture with appropriate CH_4/H_2 partial pressure ratio at which activity of carbon is high, above unity (relative to graphite). Reduction of manganese oxide by methane to manganese carbide occurs in accordance with the following reaction:

$$MnO + 10/7\ CH_4 = 1/7\ Mn_7C_3 + CO + 20/7\ H_2 \quad (1)$$

$\Delta G^o = 377{,}682 - 314.44\ T$ J/mole, [2] At standard conditions, reaction (1) proceeds spontaneously at temperatures above 928°C, while carbothermic reduction of MnO by the reaction

$$MnO + 10/7C = 1/7Mn_7C_3 + CO \qquad (2)$$

starts at 1340°C (standard conditions).

The equilibrium constant for reaction (1) is equal to 8.5 at 1000°C, 114 at 1100°C and 1075 at 1200°C. This indicates that MnO reduction to manganese carbide may have a high extent at 1000-1200°C using an appropriate gas composition.

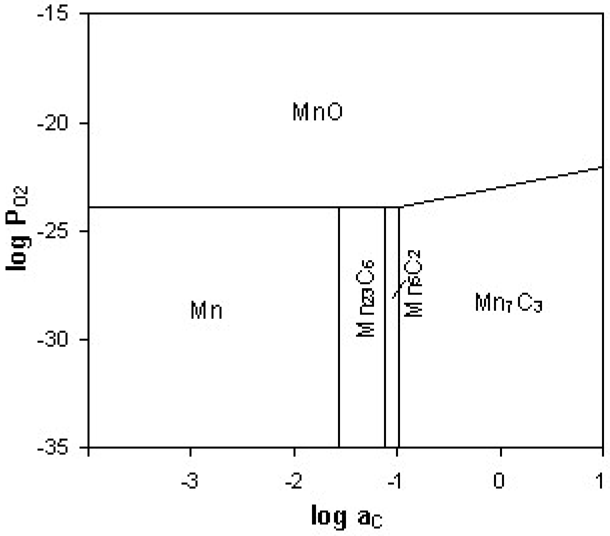

Figure 1. Stability diagram for the Mn-O-C system at 1000°C

This thermodynamic analysis shows that manganese oxide can be reduced by methane-containing gas to manganese carbide at temperatures below 1200°C when manganese ore is solid. This paper presents results of experimental study of reduction of Groote Eylandt and Wessels manganese ores by a methane-hydrogen-argon gas mixture.

2. EXPERIMENTAL SETUP AND PROCEDURE

Chemical composition of ores examined in this paper, determined by XRF, is given in Table 1.

Table 1. Compositions of Wessels and Groote Eylandt (GE) manganese ores.

Ore	Mn	SiO_2	Fe	Al_2O_3	CaO	BaO	K_2O	Na_2O	TiO_2
Wessels	48.2	3.2	11.0	0.351	5.4	0.4	0.007	0.027	0.013
GE	61.5	4.4	6.7	1.19	0.03	0.8	1.30	0.30	0.15

The Wessels ore was calcined at 1000°C under air in a muffle furnace for 2 hours and then crushed to the size fraction 0.35 – 2.0 mm. The Groote Eylandt ore was crushed and ground to different size fractions. Phase analysis showed that the ore was not homogeneous: (1) ore composition depended on the ore size, (2) it contained the separate silica phase, and (3) iron oxide was non-uniformly distributed, predominantly along the cleavages. To obtain a homogeneous ore for reduction experiments a fine powder of the ground ore (100 microns) was sintered in a muffle furnace at 1200°C for 5 hours in air. The sintered ore was then crushed and ground to 1.2 mm.

To study the effect of ore composition on the reduction behaviour, Groote Eylandt ore was doped with CaO by adding calcium carbonate ($CaCO_3$) to have 3, 6, 10 and 15 wt% CaO in the sample. The manganese ore and the $CaCO_3$ were mixed, crushed and ground. Mixed powders were sintered in a muffle furnace at 1200°C for 5 hours in air. The sintered ore was then crushed and sized to 1.2 mm.

The reducing gas was made from methane, hydrogen and argon with addition in some experiments of carbon monoxide. Before being introduced into the furnace, all the gases were cleaned using a Hydro Purge purifier to remove moisture and carbon dioxide. The hydrogen gas line had an additional activated charcoal purifier to remove hydrocarbons.

Isothermal and non-isothermal reduction experiments were conducted in a fixed bed reactor in a vertical tube electric furnace coupled with mass spectrometer and dewpoint sensor for H_2O analysis, and complemented by LECO oxygen analysis, XRD, SEM and Electron Microprobe analyses. The experimental set up and procedure are described elsewhere [3]. Surface area and pore size distribution in raw materials and reduced samples were measured by BET and Mercury porosimetry.

Oxygen removed from the sample in the reduction experiment was calculated on the basis of CO and H_2O content in the exit gas measured on-line by a dew point sensor and a mass spectrometer. CO_2 content in the off gas was negligible. The extent of reduction was determined as a ratio of oxygen removed to total initial oxygen in iron and manganese oxides.

The data obtained from the mass spectrometer and dew point sensor were first converted to the molar flow rate, using argon gas as a reference:

$$C_i = \left(\frac{V_i}{V_{Ar}} \right) \times C_{Ar} \tag{3}$$

where: V_i = volume percentage of CO or H_2O in the off gas;
C_i = molar flow rate of CO or H_2O in the off gas;
V_{Ar} = volume percentage of Ar in the off gas;
C_{Ar} = the molar flow rate of Ar in the inlet gas.

The extent of reduction (X) was determined by integrating the oxygen removal rate as:

$$X = \frac{1}{N_O} \int R_O dt \tag{4}$$

where: $R_O = C_{H2O} + C_{CO}$;
N_O = amount of reducible oxygen in the sample;
t = the reduction time.

The extent of reduction was also calculated on the basis of oxygen and carbon content analysed by LECO.

3. EXPERIMENTAL RESULTS

3.1 Reduction of Pure Manganese Oxides

In the first stage, reduction of pure manganese oxide MnO_2 by H_2-Ar gas (20 vol% H_2 and 80 vol% Ar) and CH_4-H_2-Ar gas mixtures (10 vol% CH_4, 20 vol% H_2 and Ar the balance) was studied. Reduction of MnO_2 by H_2-Ar gas started at 305 - 320^{o}C. Pure MnO_2 was completely reduced to MnO at 610 - 620^{o}C. In the non-isothermal reduction by CH_4-H_2-Ar gas (Fig. 2), MnO_2 was reduced to Mn_3O_4 and further to MnO by hydrogen at temperatures very close to the reduction by H_2-Ar gas. The reduction of MnO to manganese carbide started at 760^{o}C and was completed at about 1200^{o}C. In the process of MnO reduction to manganese carbide, only CO was detected in the gas phase.

Results of the isothermal reduction of manganese oxide by CH_4-H_2-Ar gas (15 vol% CH_4, 20 vol% H_2 and 65 vol% Ar) in the temperatures range 1000 - 1200^{o}C showed that the rate of manganese oxide reduction increased with temperature and methane content up to 15 vol% (in the range 2.5-20 vol% CH_4 at constant H_2 content of 20 vol%). Increase in the methane concentration above 15 vol% caused increased carbon deposition, which blocked the particle surface, affected the gas flow through the reactor and hindered the reduction process. Therefore, optimum methane content in the CH_4-H_2-Ar gas for the MnO reduction is 10-15 vol%. Effect of hydrogen concentration on manganese oxide reduction was quite marginal, however increase in hydrogen content decreased carbon deposition. Addition of CO to the reducing gas retarded manganese oxide reduction.

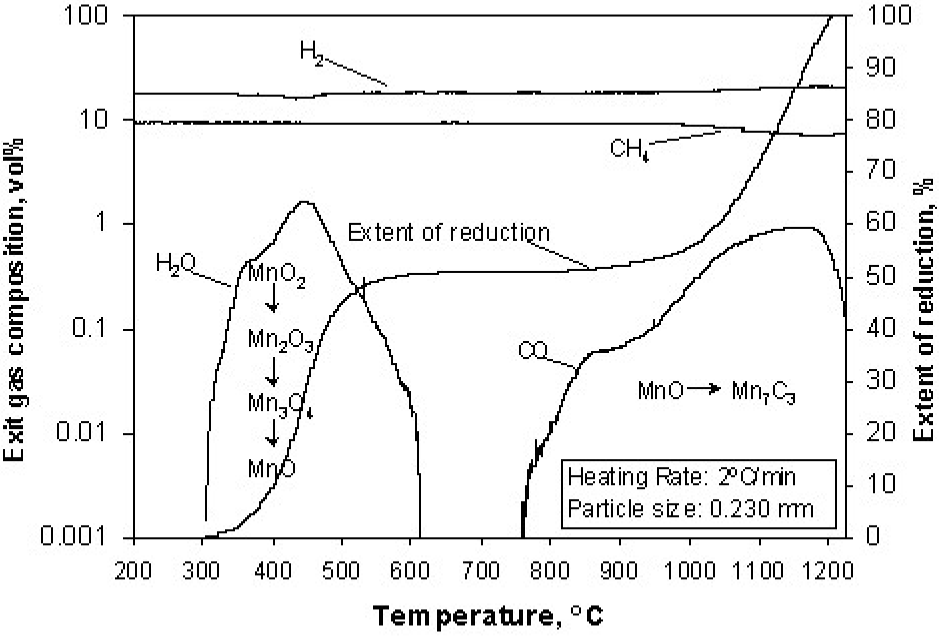

Figure 2. Non-isothermal reduction of MnO_2 by methane-hydrogen mixture (10 vol%CH_4- 20 vol% H_2 – 70 vol% Ar).

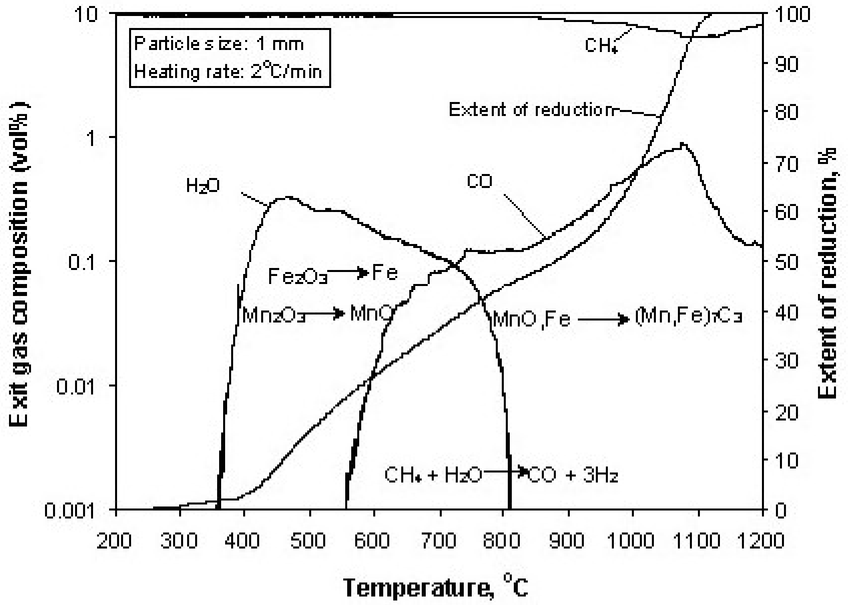

Figure 3. Non-isothermal reduction of raw Wessels manganese ore using 10 vol% CH_4, 50 vol% H_2 and 40 vol% Ar.

3.2 Reduction of Wessels Manganese Ores

In non-isothermal experiments, Wessels manganese ore was heated from 200°C to 1100-1200°C with a ramping rate of 2°C/min in different gas atmospheres: pure argon, H_2-Ar gas and CH_4-H_2-Ar gas.

Results obtained in the non-isothermal reduction, can be summarised as follows.

- During heating of Wessels ore in argon, $CaCO_3$ started to decompose at 550°C and bixbyite reduced to hausmannite at about 675°C. The extent of reduction obtained from mass-spectrometer data showed that decomposition of Mn_2O_3 to Mn_3O_4 was not complete at 1100°C.
- Reduction of the ore by H_2-Ar gas started at about 360°C; manganese oxides were completely reduced to MnO and iron oxides to metallic Fe at around 950°C.

- When CH_4-H_2-Ar gas was used (Fig. 3), iron and manganese oxides were reduced to ferro-manganese carbides. Reduction of MnO to ferromanganese carbide started at 550°C and completed at about 1150°C. Early evolution of CO at 550°C indicates that CH_4 participated in the reduction of Mn_3O_4 to MnO and reacted with water vapour in the gas phase. The formation of iron-manganese carbide was proved by the XRD analysis of a reduced sample.

The effect of temperature on the extent and rate of Wessels ore reduction studied in isothermal experiments is shown in Fig. 4. The reaction rate increased with temperature. At 1200°C, the extent of reduction was close to 100% after one hour reduction. These data were confirmed by oxygen analysis using a LECO machine. The rate of $(Mn,Fe)_7C_3$ formation increased rapidly with increasing temperature to 1150°C. Further increase in temperature to 1200°C affected the reduction rate quite marginally. However, excessive methane cracking at higher temperature hindered reduction due to carbon deposition. In the course of reduction, H_2O and CO were formed. Basically, no CO_2 related to the reduction process was detected in the reduction experiment. H_2O was registered at the early reduction stage but then decreased quickly as the reduction progressed. It could be related to reduction of manganese oxides to MnO and iron oxides to metallic iron.

The effect of methane in the gas mixture on the Wessels ore reduction is shown in Fig. 5. The methane content was varied from 2.5 to 25% at constant hydrogen content of 50% and temperature at 1100°C. The rate of reduction increased as the methane content increased to 15 vol%. Further increase in methane content had minimal effect. The final extent of reduction was close to 100% when methane content in the reducing gas was 5 vol% and above.

The effect of hydrogen content in the gas mixture was examined at 1100°C and at a constant methane content of 10 vol% CH_4. Hydrogen content in the gas mixture was varied from 10 to 70 vol%. The hydrogen concentration in the reducing gas in the range of 30-70 vol% had a slight effect on the reduction.

The influence of carbon monoxide on the reduction of Wessels ore was examined in the range of 0-5 vol% CO at 1100°C with fixed methane (10 vol%) and H_2 (50 vol%) concentrations. The addition of carbon monoxide to the reducing gas above 1.5 vol% retarded the reduction. Increase in CO content to 5% decreased the extent of reduction to below 50% after 2.5 hours of reaction. The effect of gas flowrate was investigated in the range of 0.75 NL/min to 1.5 NL/min. The weight of a sample was changed proportionately to keep the gas residence time in bed constant. The rate of reduction slightly increased with increasing flowrate from 0.75 NL/min to 1 NL/min. Further increase in gas flowrate had no visible effect on the reduction of Wessels ore. On the basis of these results, the gas flowrate was maintained at 1 NL/min.

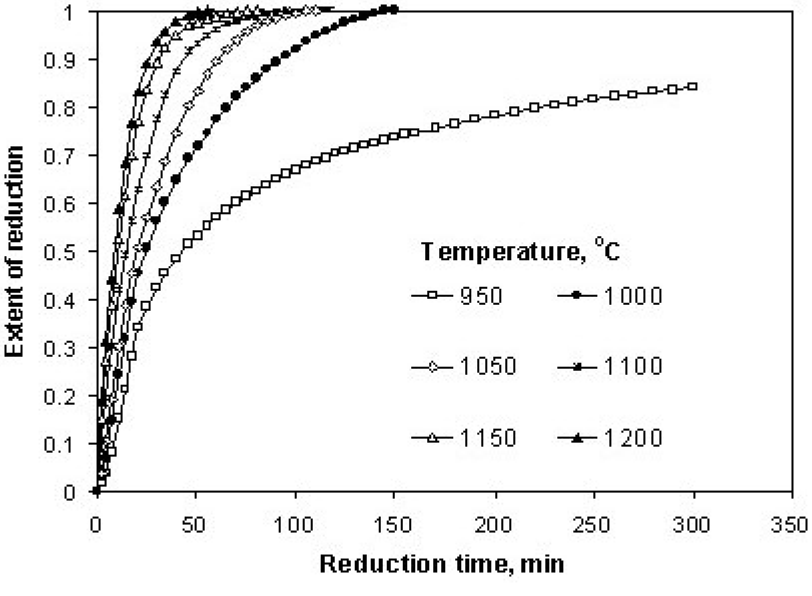

Figure 4. Reduction of Wessels ore by methane-hydrogen-argon gas mixture (10 vol% CH_4-50 vol% H_2-40 vol% Ar) at different temperatures.

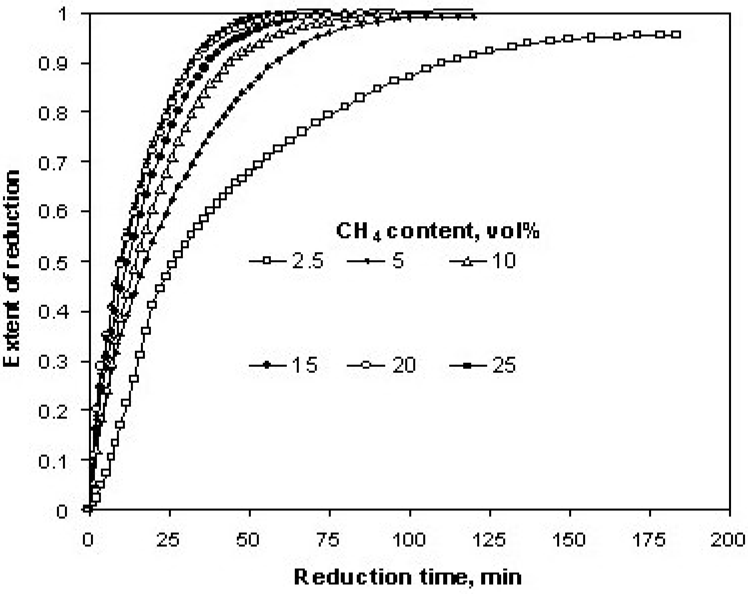

Figure 5. Reduction of Wessels ore by CH_4-H_2-Ar gas mixture with different methane content at 1100°C (H_2 content was constant at 50 vol%).

The rate and extent of reduction was practically independent of the particle size in the range of 350 µm to 2.0 mm at 1100°C, which can be related to the high porosity of the ore.

Samples reduced at 1000, 1100 and 1200°C were subjected to XRD analysis. X-ray diffraction patterns at various stages of reduction of Wessels manganese ore at 1200°C are shown in Fig. 6. Formation of ferromanganese carbide was completed in 120, 60 and 45 minutes at 1000, 1100 and 1200°C, respectively. Reduced Wessels ore showed X-ray diffraction patterns similar to reduced pure MnO. The ferromanganese carbide was identified as $(Mn,Fe)_7C_3$.

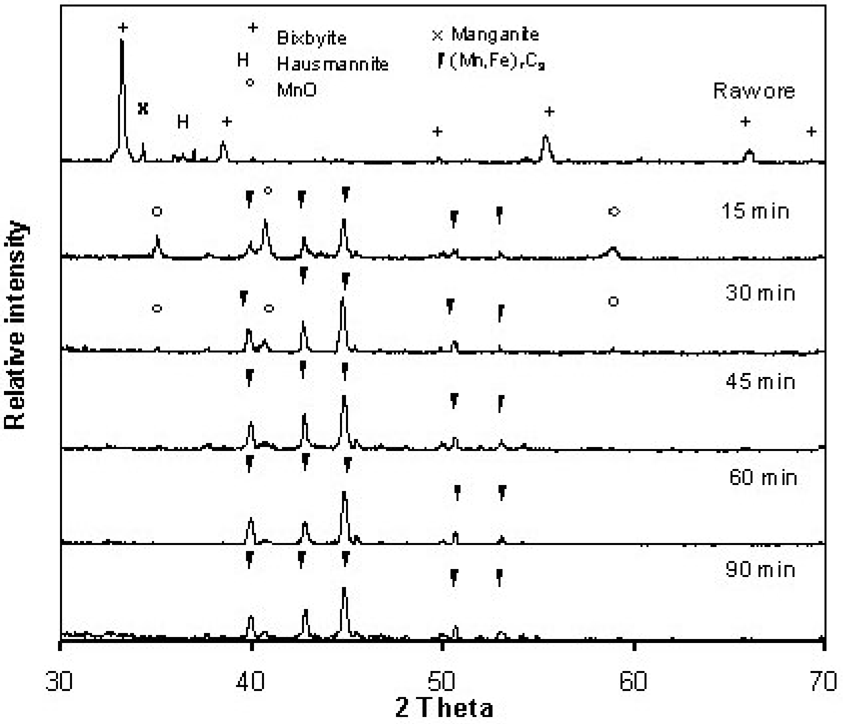

Figure 6. X-ray diffraction patterns of Wessels ore at different stages of reduction by CH_4-H_2-Ar gas mixtures at 1200°C.

3.3 Reduction of Groote Eylandt manganese ore

Morphology of Groote Eylandt (GE) manganese ore was different from Wessels ore. SEM analysis detected two phases in the ore matrix, distinguished by colour. The major (light) phase had higher manganese content, while the second (dark) phase had higher potassium, iron, silicon and aluminium. Silicon and iron content in both phases were lower than

determined by the bulk analysis (2.05% Si and 6.72% Fe). This means that only a fraction of Si and Fe was associated with manganese in the ore matrix. Silica was present in the form of inclusions or sand nodules. Discrete portions of iron were observed in the form of hematite (Fe_2O_3).

There were points in the reduced ore matrix where iron was not detected. SEM and optical microscopy of a sample reduced by hydrogen-argon mixture at 1150^oC confirmed that iron oxide was predominantly detected along the cleavages. It was observed that ore composition depends on the ore size.

To obtain a homogeneous ore for isothermal reduction experiments, fine ground ore (100 microns) was sintered in a muffle furnace at 1200^oC for 5 hours in air. The sintered ore was then crushed and ground to 1.0 mm. As a result of sintering, the grain size increased and a glassy phase structure was formed in the sintered ore. Microprobe analysis of the sintered ore revealed that the glassy phase had higher Si, Ba and Al concentration but lower Mn and Fe contents compared to the major phase. Total oxygen content decreased after sintering as a result of MnO_2 decomposition; this was confirmed by the LECO analysis. Sintered ore exhibited a more uniform iron distribution in the ore matrix, predominantly observed along the grain boundaries.

There was a slight decrease in total pore area when the ore was heated in argon or reduced in hydrogen and a significant decrease in pore area when it was sintered at 1200^oC.

The reduction behaviour of Groote Eylandt manganese ores was also studied in non-isothermal and isothermal experiments. Temperature-programmed non-isothermal experiments were performed under pure argon, hydrogen-argon and methane-hydrogen-argon gas mixture. The reduction by H_2-Ar gas started producing water at around 230^oC. The extent of reduction achieved 52% which is equivalent to the reduction of MnO_2 to MnO and Fe_2O_3 to Fe. XRD analysis also revealed only MnO and Fe phases after reduction.

The first stages in non-isothermal reduction of GE ore by CH_4-H_2-Ar gas mixture which produced H_2O were similar to reduction by H_2-Ar gas. Hydrogen reduced iron oxides to metallic iron and higher oxides of manganese to MnO. Methane reduced MnO to manganese carbide. Evolution of CO at 570^oC can be related to a reaction of methane with H_2O or reduction of Mn_3O_4 to MnO. Ferromanganese carbide started to form at a higher temperature at around 760^oC.

Complete reduction of the ore was not achieved due to blockage of a porous plug at about 1160^oC. The blockage was not encountered during the non-isothermal reduction of Wessels ore and pure MnO_2. The blockage was caused by slag softening and carbon deposition. Accumulation of carbon in the sample can be observed by the gradual increase of the gas pressure in the gas inlet. Iron present in the ore catalysed the decomposition of methane.

The effect of temperature on the reduction of GE ore was investigated using gas containing 10 vol% CH_4, 50 vol% H_2, and 40 vol% Ar in isothermal experiments. Fig. 7 shows the extent of reduction *vs* time at different temperatures. The reduction rates of Groote Eylandt manganese ore increased with increasing temperature from 1000 to 1050^oC. It was practically independent of temperature in the temperature range 1050-1100^oC, and decreased with further increase in temperature. The optimum temperature for the reduction of sintered GE ore was 1050-1100^oC at which the extent of reduction was more than 90%.

Sintering of the ore and carbon deposition during the reduction reduced the reduction rate significantly due to a decrease in surface area. Above 1050^oC there was a rapid increase in pore size and a significant decrease in total pore area with increasing temperature. Examination of a variation of average pore diameter and total pore area with reduction temperature showed that fine pores were eliminated with increasing reduction temperature.

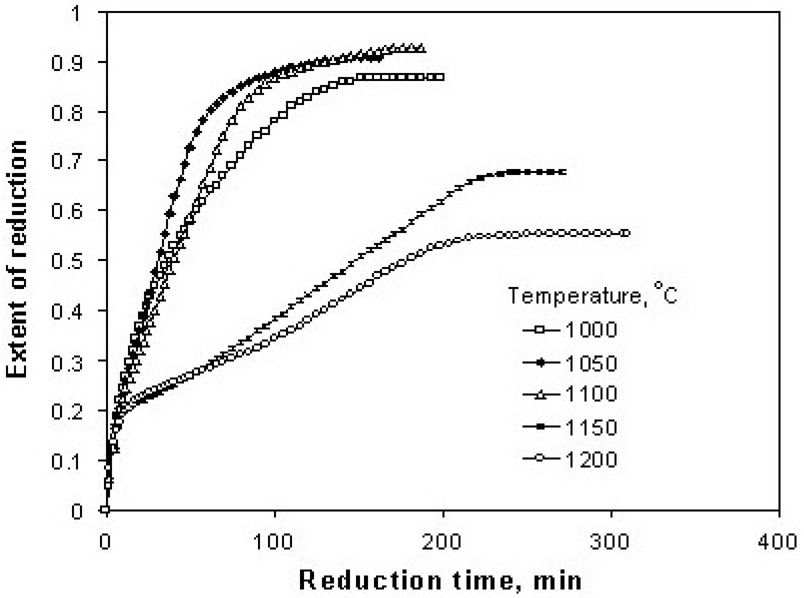

Figure 7. Extent of reduction of sintered Groote Eylandt Mn ore by methane-hydrogen gas mixture (10 vol% CH_4-50 vol% H_2-40 vol% Ar) at different temperatures.

The relatively low softening temperature of GE ore and predisposition to sintering are related to higher silica content in comparison with the Wessels ore and formation of low melting silicates. To study the effect of ore chemistry further, the GE ore was doped with CaO. Ground samples of Groote Eylandt manganese ore with CaO concentrations of 3, 6, 10 and 15 wt% were sintered in air at 1200°C for 5 hours. Three grams of a sample (1 mm particle size) were isothermally reduced at 1050-1200°C by methane containing gas mixtures (10 vol% CH_4-50 vol% H_2-40 vol% Ar). The rate of MnO reduction by methane was only slightly affected by CaO addition at 1050-1100°C. The influence of CaO was more significant in experiments at 1150-1200°C (Fig. 8). An addition of CaO to the Groote Eylandt manganese ore significantly increased the rate and extent of reduction at elevated temperatures. However, the extent of reduction did not reach a completion, and the maximum degree of reduction was only about 90 %. The addition of 10 wt% CaO to the ore brought the highest increase in the rate of reduction.

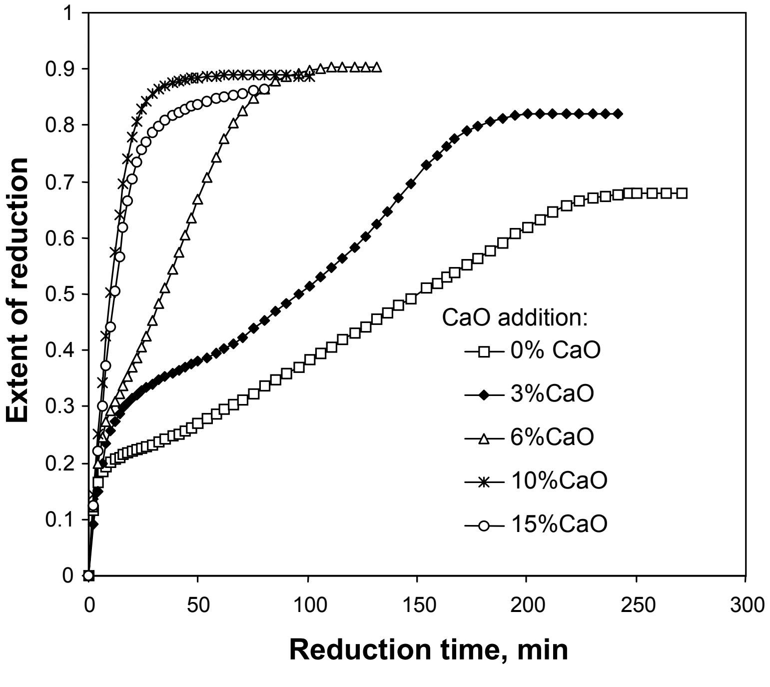

Figure 8. Effect of CaO addition on the rate and extent of reduction of Groote Eylandt ore by methane-hydrogen-argon mixture (10 vol% CH_4-50 vol% H_2-40 vol% Ar) at 1150°C

Increasing CaO addition to 15 wt% slightly decreased the rate of reduction compared to 10 wt% CaO except reduction at 1200^{o}C. At 1050^{o}C addition of 15 wt% CaO slightly decreased the extent of reduction even compared to pure GE ore.

XRD of samples reduced by methane-hydrogen gas mixtures at 1150 and 1200^{o}C detected carbide $(Mn,Fe)_7C_3$ and tephroite, which was not observed in reduced Wessels ore. In the reduction of GE ore doped with 10-15 wt% CaO, tephroite was not detected in the reduced sample. Phase composition of samples reduced at 1050^{o}C was not affected by CaO addition.

4. DISCUSSION

The driving force for reduction of manganese oxide to manganese (ferromanganese) carbide is high carbon activity in CH_4-H_2-Ar gas. The carbon activity in the CH_4-H_2 gas is well above unity (relative to graphite), and increases with temperature. This makes the reduction of manganese ore by methane-containing gas faster than in the conventional carbothermal reduction process.

Fig. 9 presents the reduction curves for Wessels ores reduced by graphite (carbothermic reduction) at 1300^{o}C [4] and by CH_4-H_2-Ar gas mixtures at 1200^{o}C. It is seen that the reaction rate at the first stage of reduction (first 6-10 minutes) was the same. This is expected since the first stage of reduction comprises the reduction of higher manganese oxides to manganous oxide (MnO) and iron oxides to metallic iron which proceeds quickly. However, at the second stage, the reaction of MnO with solid carbon is very slow. Reduction of Wessels ore by CH_4-H_2-Ar gas at 1200^{o}C is much faster than by graphite in argon or CO at 1300^{o}C. This makes the methane containing gas mixtures an effective reducing agent of manganese ores to ferromanganese.

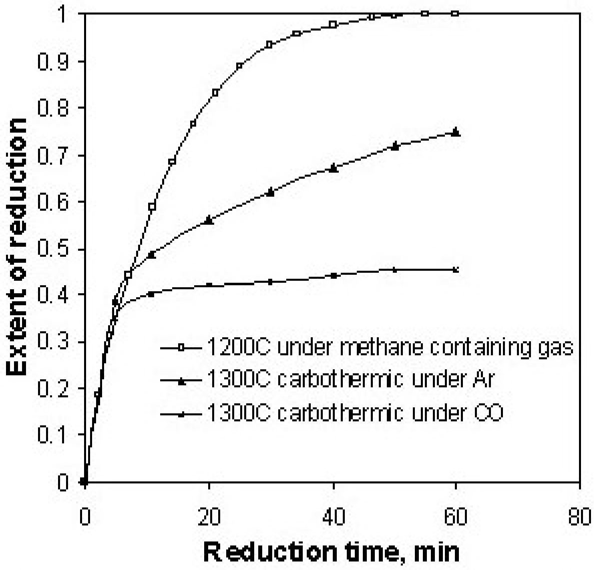

Figure 9. Reduction curves for Wessels ores reduced by graphite in CO and Ar atmospheres at 1300°C [4] and by CH_4-H_2-Ar gas.

The initial rate of reduction of Wessels and GE ores was independent of temperature. Only when the extent of reduction exceeded 20% the rate of reduction was affected by temperature. The reduction rate of pure MnO and Wessels ore by CH_4-H_2-Ar gas mixtures increased with increasing temperature in the whole experimental temperature interval. However, the rate of MnO reduction from the Groote Eylandt ore increased in the interval 1000-1100^{o}C and decreased with further increase in temperature to 1150-1200^{o}C. During this stage MnO formed as a result of higher manganese oxides reduction combined with SiO_2 and Al_2O_3 producing a low melting temperature slag, containing K_2O. This slag limited an access of the reducing gas to the ore interior and retarded the reduction. Surface area of the ore also reduced as a result of sintering. The total pore area decreased sharply from 1 m^2/g at 1050^{o}C to 0.13 m^2/g at 1100^{o}C.

A comparison of the Wessels ore and Groote Eylandt ore compositions shows the following:

- Wessels ore contains less SiO_2 (3.2%) and Al_2O_3 (0.351%) compared to Groote Eylandt manganese ore with 4.38% SiO_2 and 1.19% Al_2O_3.
- Wessels ore has higher CaO, 5.4% compared to 0.03% CaO in Groote Eylandt ore.
- Wessels ore contains 74 ppm K_2O and 275 ppm Na_2O, what is less than the amount of alkali oxides (1.32% K_2O and 0.3% Na_2O) in Groote Eylandt ore.

The reduction rate of MnO by CH_4-H_2-Ar gas was observed to be much greater for the Wessels ore than that for Groote Eylandt manganese ore. The Wessels ore was reduced at 1100°C by 70% in 25 min, while it took 60 minutes to reduce the Groote Eylandt ore under the same conditions. The extent of reduction of Groote Eylandt ore at higher temperatures (1150-1200°C) under the same conditions was less than 30%. Such reduction behaviour was caused by tephroite (Mn_2SiO_4) formation. When the temperature of the partially reduced Groote Eylandt ore was increased above 1100°C, liquid manganese silicate formed, which was fluxed by alumina and basic (particularly alkali) oxides. Fluxing by alumina lowered the liquidus temperatures of MnO-SiO_2 eutectic from 1250°C to 1140°C.

When the Groote Eylandt ore was doped with CaO, a dramatic increase in the reduction rate was observed. At 1100°C, 70% of reduction of the Wessels ore was achieved in 25 minutes while it took only 16 minutes to reduce the Groote Eylandt ore doped with 10 wt % CaO to the same extent. The addition of CaO increases the melting point of the slag preventing the liquid slag formation at experimental temperatures.

During sintering of the Groote Eylandt ore mixed with $CaCO_3$, the evolution of CO_2 as a result of $CaCO_3$ decomposition increased porosity of the sintered ore. Thus, Groote Eylandt ore doped with 10-15 wt% CaO had slightly higher reduction rate than Wessels ore (5.4 wt% CaO) at 1100-1200°C. Effect of temperature on reduction of Groote Eylandt ore doped with CaO was about the same as on the reduction of Wessels ore where increased temperature enhanced the reduction rate. The increase in the reduction rate of CaO doped Groote Eylandt ore was more significant at 1150-1200°C compared to 1050-1100°C. Nevertheless, addition of CaO dilutes the ore with respect to MnO and decreases its mole fraction.

The reduction rate of pure manganese oxide and manganese ores increased with increasing methane content in the reducing gas from 2.5 to 15 vol%, but further increase to 20-25 vol% CH_4 had no effect on the reduction rate. However, increase in methane content increased the free carbon content in the sample, particularly in the Wessels and Groote Eylandt manganese ores, where iron content catalysed the methane decomposition. This retarded the ore reduction.

Rate of reduction of pure MnO and MnO from manganese ore was slightly affected by hydrogen content when the methane concentration was fixed. The increase in reduction rate with increasing hydrogen content might be due to the suppression of solid carbon deposition. Hydrogen does not reduce MnO to Mn and therefore its role is to control the carbon activity in the gas phase. However, in the case of manganese ore reduction, hydrogen reduced the higher manganese oxides to MnO and iron oxides to metallic Fe and at the same time controlled the carbon activity in the gas phase.

The addition of carbon monoxide to the reducing gas retards the reduction of pure MnO and manganese ores. The extent of reduction of Wessels ore by reducing gas containing 5 vol% CO at 1100°C was only slightly above 40% in about 3 hours. The reactions of the first reduction stage, $Mn_3O_4 \rightarrow MnO$ and $Fe_3O_4 \rightarrow Fe$, were not affected by the increasing CO partial pressure. However, CO had a great effect on the second stage of manganese ore reduction, in which MnO was reduced to $(Mn,Fe)_7C_3$.

An increase in the temperature and methane concentration in the reducing gas increases the rate of methane cracking. The carbon starts to deposit when the rate of free carbon (graphite) formation exceeds the rate of MnO reduction and manganese carburisation, which consume carbon. The amount of solid carbon deposited increased with time.

Mechanism of reduction by methane-containing gas is different from the mechanism of carbothermal reduction. Solid carbon deposited as a result of methane cracking had a retarding effect on the reduction process. It should also be mentioned that deposition of solid carbon was mainly observed after completion of the reduction process, while in the course of reduction it was quite marginal.

5. CONCLUSIONS

In the reduction of pure MnO and manganese ores by CH_4-H_2-Ar gas, manganese oxides are reduced to manganese carbide by the reaction, given in equation (1):

$$MnO + 10/7\ CH4 = 1/7\ Mn7C3 + CO + 20/7\ H2 \qquad (5)$$

High reduction extent and rate were provided by high carbon activity in the reducing gas, which was in the range of 15-50 depending on temperature and gas composition. At 1200°C, reduction of Wessels ore by CH_4-H_2-Ar gas containing 10 vol% CH_4 and 50 vol% H_2 was close to completion in less than 50 min.

The rate of reduction of pure manganese oxide and Wessels ore increased with increasing temperature in the range 950-1200°C and methane content up to 10-15 vol% CH_4. Further increase in methane content above 15 vol% had a slight effect on the rate of reduction. Increasing hydrogen content above 20 vol% favours the reduction process.

Addition of CO to the reducing gas strongly retarded the reduction process. Solid carbon deposited as a result of the methane cracking, blocked access of the reducing gas to the oxide, and retarded MnO reduction. Methane cracking was enhanced by an increase in reduction temperature and methane content in reducing gas, and with iron addition.

The reduction and carburisation rates of Groote Eylandt manganese ores increased with increasing temperature from 1000 to 1100°C and decreased with further increase in temperature. The decrease in rates and extent of reduction at higher temperature, particularly at 1150-1200°C, was due to the formation of liquid silicate slag. Alkali oxides in Groote Eylandt ore lower the melting temperature of the ore. An addition of lime (10-15 wt% CaO) to the Groote Eylandt manganese ore increased the melting temperature of slag and significantly increased the rate and extent of reduction at elevated temperature.

6. REFERENCES

[1] Ostrovski, O., Olsen, S.E., Tangstad, M., and Yastreboff, M.M. "Kinetic Modelling of MnO Reduction from Manganese Ore" *Canadian Metallurgical Quarterly*, 2002, 309-318.

[2] Knacke O., Kubaschewski O. and Hesselmann K. *Thermochemical Properties of Inorganic Substances I*, Springer-Verlag, Second Edition, 1991.

[3] Zhang, G. and Ostrovski, O. "Reduction of Titania by Methane-Hydrogen-Argon Gas Mixtures", *Metallurgical and Materials Transactions B*, 2000, 129-139.

[4] Akdogan, G., and Eric, R.H. "Kinetics of the solid-state carbothermic reduction of Wessels manganese ores", *Metallurgical and Materials Transactions B*, 1995, 13-24.