CARBOTHERMAL SOLID STATE REDUCTION OF MANGANESE ORES

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SYNOPSIS

Carbothermal reduction of manganese oxides and manganese ores in the solid state was studied in hydrogen, helium and argon at different temperatures, ore compositions and carbon to manganese oxide ratios. Wessels ore (South Africa) and two grades of the Groote Eylandt ore (Australia) with different level of impurities were examined. Ores were characterised by XRD, X-ray fluorescence, optical microscopy and scanning electron microscopy. Isothermal and temperature programmed carbothermal reduction experiments were conducted in a fixed bed reactor in a vertical tube furnace, with on-line monitoring of gas composition by the CO-CO_2 infrared sensor. The reduced samples were characterised by XRD, SEM and LECO analyses. Extent of reduction was calculated using data on the off-gas composition, and LECO carbon and oxygen contents in the reduced sample. Manganese oxides in the ore were reduced to α-Mn and carbides $Mn_{23}C_6$ and Mn_7C_3 depending on the carbon to ore ratio. The reduction rate of manganese ores in hydrogen was higher than in helium and argon.

***Key words**:* Manganese, Carbothermal Reduction, Hydrogen, Argon, Carbon Monoxide, Helium, Kinetics.

1. INTRODUCTION

Carbothermal reduction of manganese ore is the major industrial method for processing of manganese ore, and has been intensively studied [1-12]. It is well established that manganese oxide is reduced quite slowly in the solid state. That is why in the industrial production of manganese alloys in blast or electric ferroalloy furnaces, the reduction/smelting temperature is around 1500°C, at which manganese oxide is reduced from the molten slag. However, manganese oxide in manganese ore exists in the form of a separate phase [6-8, 10]. In the smelting reduction of manganese ore, manganese oxide is firstly dissolved into the molten MnO-SiO_2-Al_2O_3-CaO-MgO slag, and then is reduced from the slag. Reduction of manganese oxide from the slag is strongly retarded by silica, and is slower than the reduction of pure manganese oxide [7, 8]. Reduction or pre-reduction of manganese ore in the solid state, if it is implemented at a reasonable rate, can improve efficiency of processing of manganese ore. A study of the solid-state manganese ore reduction is the aim of this paper.

Effects of temperature, ore composition and size are quite well established [1, 3, 5, 7, 8, 10-15]. The effect of gas atmosphere on the carbothermal reduction of manganese oxide and manganese ore has been studied to a lesser extent. Ding [16] examined the effect of the partial pressure of CO on the manganese ore reduction. He stated that decreasing the CO partial pressure by about two thirds is equivalent to a temperature increase of 60-70 degrees. Skjervheim and Olsen [12] also found that lowering the CO partial pressure enhanced the rate of reduction. Eric and Burucu [3] compared rates of MnO reduction by graphite in different gas atmospheres; in argon, carbon monoxide, carbon dioxide, and by CO. They showed that the argon and carbon combination gave the greatest rate and extent of reaction, followed by the other systems in the order above. Data obtained by Terayama and Ikeda [11] for carbothermal MnO reduction in helium showed that MnO is reduced much faster in helium than in argon. Similar results were obtained by Yastreboff *et al*. [9] for MnO, manganese ore and ferromanganese slag. The strong response to changing the atmosphere to a different inert gas with different diffusivity provides an insight not only to the reaction mechanism, but also to the identification of limiting stages.

This paper examines carbothermal reduction of MnO and manganese ores in argon, helium and hydrogen. No previous work on carbothermal reduction of manganese oxides or manganese ore in hydrogen has been published to our knowledge. The paper presents experimental results on the carbothermal reduction of MnO, Wessels ore (South Africa) and two grades of the Groote Eylandt ore (Australia).

2. EXPERIMENTAL

Samples were made by mixing pure MnO or manganese ore with graphite. Manganese monoxide was supplied by Aldrich Chemical Company, Inc. The manganese monoxide was in powder of -60+170 mesh, with a purity of > 99%. Synthetic graphite (CAS 7782-42-5) in a powder of <20 microns was mechanically mixed with manganese oxide MnO with varied MnO/C.

The investigated manganese ores were Groote Eylandt (Australia) and Wessels (South Africa) ores. Two grades of Groote Eylandt were studied: Groote Eylandt Premium Sand with high silica content (GE-PS) and Groote Eylandt Premium Fines (GE-PF). Manganese ores were preheated in air at 1000 C for 3 hours. Results of XRF and LECO (oxygen) analyses of preheated ores are shown in Table 1. The examined ores had a fraction of +45-150 m.

Reduction experiments were conducted in an alumina reactor in the vertical electric furnace. The furnace gas atmosphere was made from pure hydrogen, helium or argon. Brooks mass flow controllers with electronics were used to regulate gas flow rates. A powder sample was placed into a graphite crucible with 10 mm diameter and 21 mm height. The average sample mass was 1.00 g. The exit gas was analysed using CO-CO2 Infrared Analyser and dew point monitor. Phase composition of samples was characterized by X-ray Siemens D5000 diffractometer with Ni-filtered Cu K radiation.

Table 1: Chemical analysis of preheated ores, wt%

Element	Wessels	GE-PF	GE-PS
Mn	49.20	59.27	42.26
Fe	10.15	3.58	5.06
O	30.04	30.32	32.61
Si	1.772	2.25	14.06
Al	0.727	1.78	2.86
Ca	5.405	0.10	0.10
Mg	0.3987	0.09	0.08
K	-	0.92	0.53
Ba	0.6645	0.43	1.13
P	0.0353	0.07	0.08
Ti	0.0266	0.08	0.19
Zn	0.0206	0.02	0.02
V	-	0.02	0.02
Sr	-	0.04	-
Cd	0.0111	-	-
Other	1.5567	1.05	0.99
Total	**100**	**100**	**100**
Mn/Fe ratio	**4.85**	**16.5**	**8.34**

3. RESULTS

3.1 Carbothermal reduction of pure MnO in different gas atmospheres

Carbothermal reduction of pure MnO in hydrogen, helium and argon was studied in the temperature range 1050-1400^{o}C. Reduction in hydrogen was examined at different MnO/carbon molar ratios. Figure 1 shows reduction curves at 1200^{o}C for the MnO/C molar ratio in the range 1/0.34 to 1/2. Reduction behaviour was not affected by the MnO/C ratio, when it was below 1/1.22. However, this ratio had a strong affect on the phases formed in the course of reduction (Fig. 2). Table 2 summarises results of XRD analysis (Fig. 2) of samples obtained in the MnO reduction in the temperature range 1200 to 1300 ^{o}C with different MnO/C ratio.

For samples with MnO/C ratio more than 1 the main phase was MnO; only a small amount of manganese carbide $Mn_{23}C_6$ and $\alpha - Mn$ was observed. When the molar MnO/C ratio was in the range of 1 to 1/2 or smaller no oxide phase was detected; the main phases were $\alpha - Mn$ and $Mn_{23}C_6$. Reduced samples with MnO/C

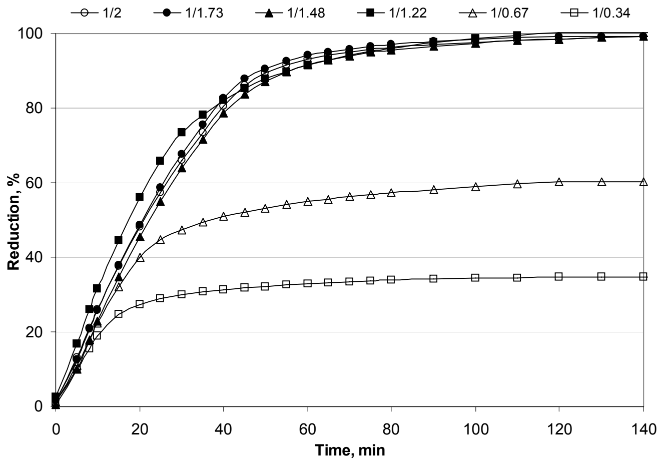

Figure 1: Carbothermal reduction of MnO samples with different MnO/C molar ratios at 1200 °C in hydrogen

less than 1/1.5 contained only carbide phase Mn_7C_3 (Table 2). No residual carbon was observed in a sample produced in the reduction with MnO/C ratio 1/1.3 and above. The stoichiometric MnO/C molar ratio for complete conversion of MnO to Mn_7C_3 is 1/1.43 (7/10).

The XRD examination of samples with MnO/C ratio below the stoichiometric value in the course of reduction revealed (Fig. 3) that reduction of MnO proceeded to $Mn_{23}C_6$ through the high carbon manganese carbide Mn_7C_3. The final product depended on the MnO/C ratio (see Table 2) and was independent of the gas atmosphere. For a sample with MnO/C=1/1.3, the formation of Mn_7C_3 carbide was completed in 60 min, when the degree of reaction reached 91% reduction, and all carbon was consumed. This reduction stage can be presented by the equation:

Table 2: Phases formed in the carbothermal MnO reduction with different Mn/OC ratios

MnO/C ratio	>1	1/1.1	1/1.3	1/1.5	½
Final products	MnO, α -Mn, $Mn_{23}C_6$	a-Mn, $Mn_{23}C_6$	$Mn_{23}C_6$	Mn_7C_3, C	Mn_7C_3, C

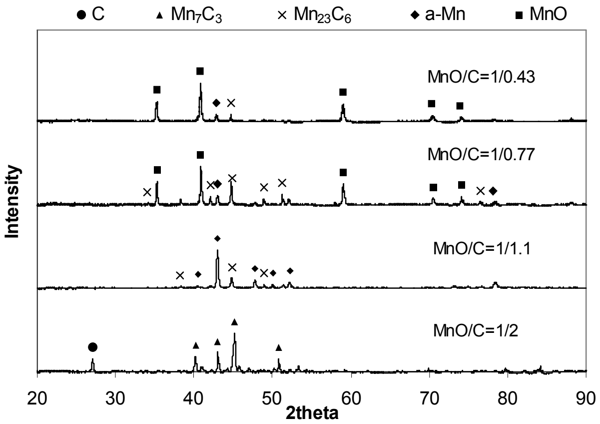

Figure 2: XRD patterns of reduced MnO samples with different MnO/C ratios in hydrogen and helium in the 1200 to1300 °C

$$MnO + 1.3C = 0.13Mn_7C_3 + 0.91CO + 0.09MnO \qquad (1)$$

Further reduction proceeded in accordance with the equation (2):

$$0.09MnO + 0.097Mn_7C_3 = Mn_{23}C_6 + 0.09CO \qquad 2)$$

Reduction curves for carbothermal reduction of MnO with MnO/C ratio of 1/1.3 in hydrogen in the temperature range 1050-1400°C are presented in Figure 4. In all gases, reduction rate increased with increasing temperature

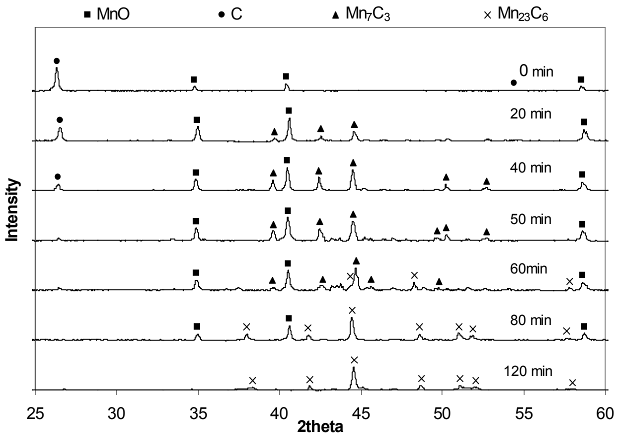

Figure 3: XRD patterns taken at various stages of MnO reduction in hydrogen with MnO/C ratio 1/1.3 at 1200° C

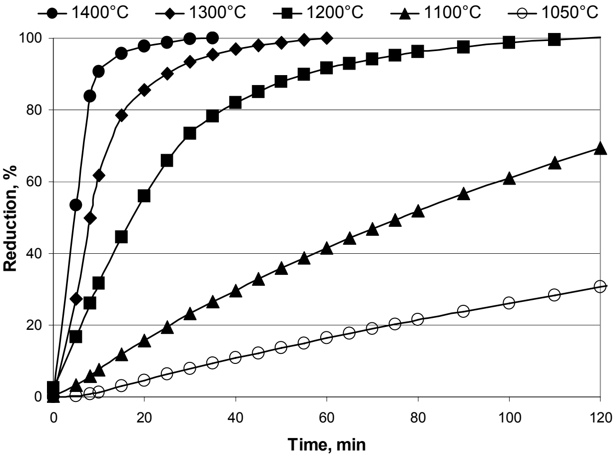

Figure 4: Carbothermal reduction of MnO at different temperatures in hydrogen, MnO/C ratio 1/1.3

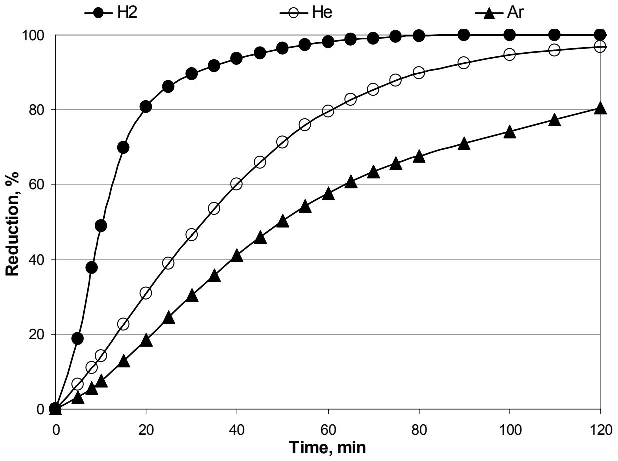

Figure 5:Reduction curves for samples with MnO/C = 1/1.3 at 1275 °C in different gas atmospheres

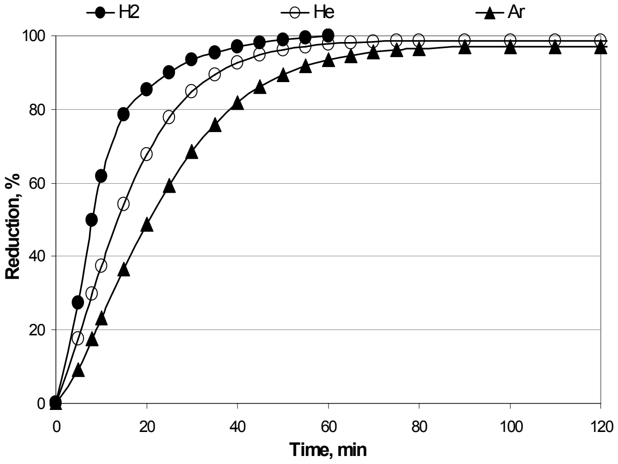

Figure 6: Reduction curves for samples with MnO/C = 1/1.3 at 1300 °C in different gas atmospheres

Effect of gas atmosphere on MnO reduction at different temperatures is shown in **Figures 5-7**. Reduction was the fastest in hydrogen and slowest in argon, however, effect of gas atmosphere depended strongly on the temperature. Reduction in argon and helium at temperatures 1275°C and below was slow and incomplete; only reduction in hydrogen was close to completion at 1200°C. However, the difference in the reduction behaviour in different gases decreased with temperature. At 1400°C, reduction curves obtained in hydrogen and helium were almost identical (**Fig. 7**), although reduction in argon was slower than in H_2 and He.

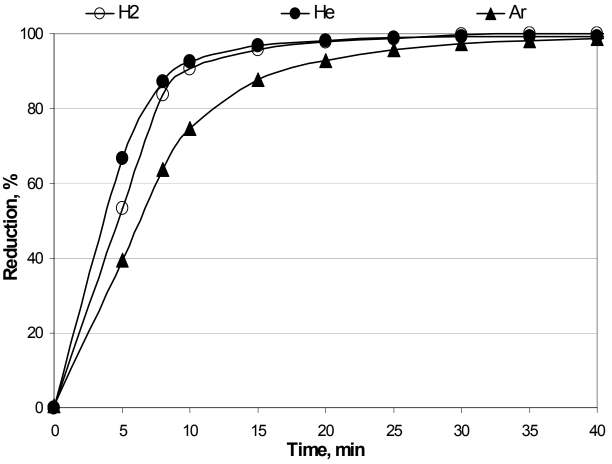

Figure 7: Reduction curves for samples with MnO/C = 1/1.3 at 1400 °C in different gas atmospheres

3.2 Carbothermal reduction of manganese ores

In the reduction of manganese ore, the effect of the ore to carbon ratio (by mass) was studied at 1200°C in the hydrogen gas atmosphere. Reduction curves are presented in Figures 8-10. Reduction curves for the Wessels ore were in a relatively narrow band for the carbon content in the ore-carbon mixture in the range 12-30 wt%.

Effect of carbon content on the reduction of GE ores was quite minor when the carbon content was above 20-22 wt%. However, the carbon content affected strongly the phase composition, which is shown in Table 3.

Reduction curves for Wessels, GE-PF, GE-PS ores and manganese oxide in hydrogen, helium and argon at 1100°C and 1200°C are shown in **Figures 11** and **12** respectively. At constant temperature, rate of reduction depended on the type of the ore and the gas atmosphere. Under identical conditions, rate and extent of reduction of Wessels ore were higher than of GE ores and of pure MnO oxide. All ores reduced faster in hydrogen than in helium, and reduction in helium was faster than in argon. Reduction of manganese ores in helium and argon at temperatures 1100°C and 1200°C and, in hydrogen at 1100°C was incomplete.

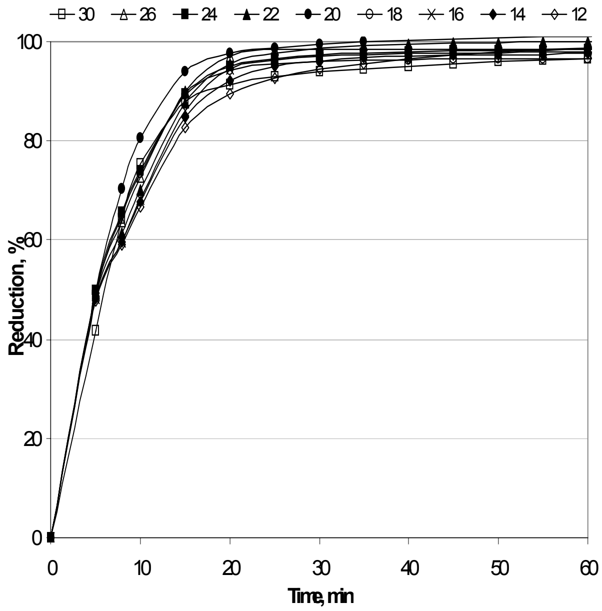

Figure 8: Carbothermal reduction of Wessels ore with different carbon content (wt%) at 1200 °C in hydrogen

4. DISCUSSION

It is accepted that carbothermal reduction by solid carbon proceeds via a gas phase. The overall reaction of MnO reduction by carbon

$$7MnO+10C=Mn_7C_3+7CO \quad (3)$$

is presented as a sum of three reactions

$$MnO+CO=[Mn]+CO_2 \quad (4)$$

$$CO_2+C=2CO \quad (5)$$

$$7Mn + 3C = Mn_7C_3 \quad (6)$$

The rate of the overall MnO reduction is suggested to be limited by the interfacial Boudouard reaction [1, 11], or by transport of CO_2 within the porous bed of the solid reactant mixture to the carbon particles [2]. At high temperatures, when MnO is reduced from the molten slag, direct graphite-molten slag reaction may dominate in the reduction processes.

The rate of MnO and manganese ore carbothermal reduction is the fastest in hydrogen, and is faster in helium than in argon. Strong effect of the gas atmosphere on the rate of manganese oxides reduction indicates that external and internal mass transfer of gaseous reactants may play an important role in the reduction kinetics. The difference between Ar and He is the degree of resistance that they impress onto the diffusivity of

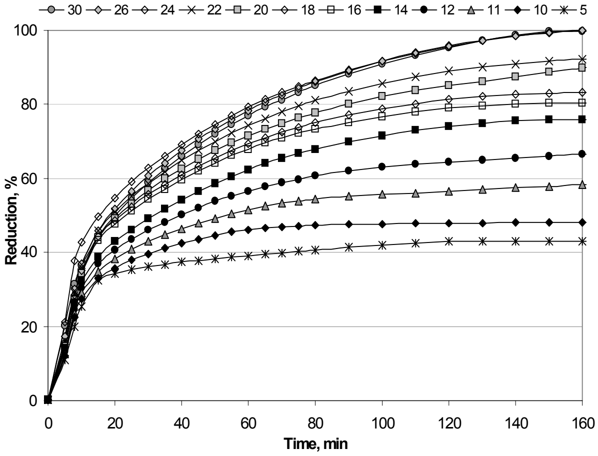

Figure 9: Carbothermal reduction of GE-PS ore with different carbon content (wt%) at 1200 °C in hydrogen

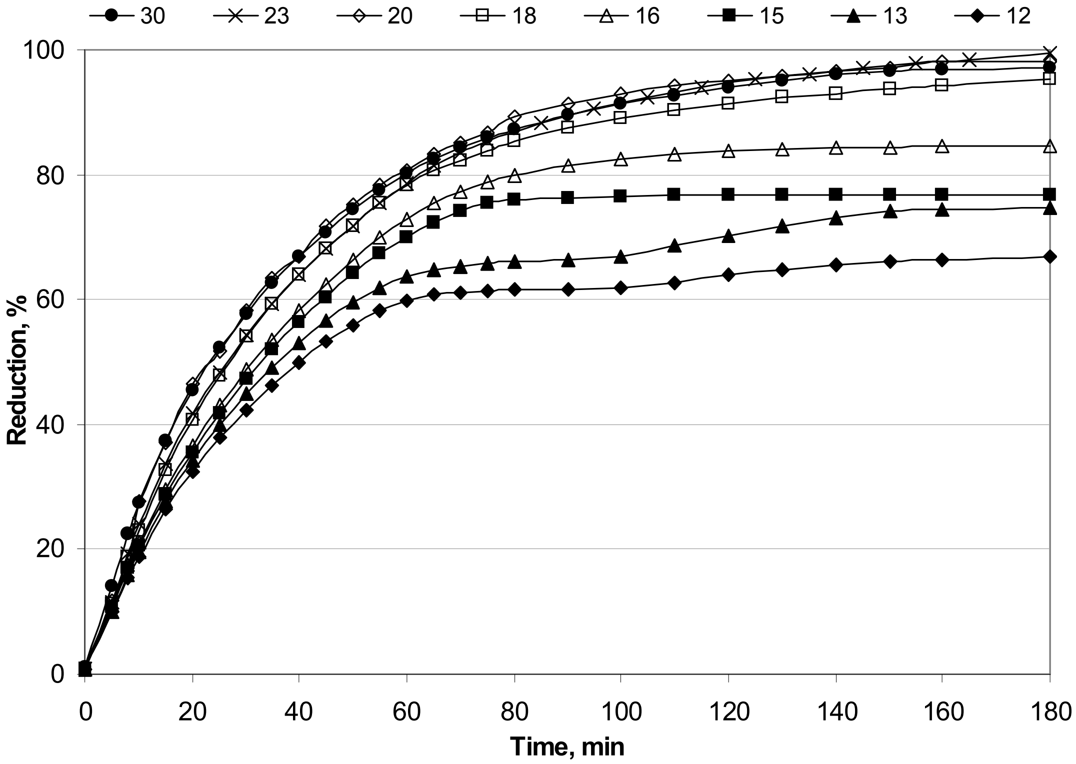

Figure 10: Carbothermal reduction of GE-PF ore with different carbon content (wt%) at 1200 °C in hydrogen

other gaseous species. Diffusivity of CO in helium and argon, calculated using the Chapman-Enskog formula [17] at 1400°C and 1 atmosphere is 16.9 cm^{2}sec-^{1} and 3.6 cm^{2}sec-^{1} respectively. The difference is a factor of 4.7.

Phase composition of reduced manganese ores samples with different carbon content at 1200°C in hydrogen

wt%C	Wessels	GE-PS	GE-PF
5	-	Mn_2SiO_4	-
11		Mn_2SiO_4, $MnSiO_3$, $Mn_{22.6}Si_{5.4}C_4$, $(Mn,Fe)_5SiC$	MnO, Mn_2SiO_4, $(Mn,Fe)_{23}C_6$
12 **13**	$Fe_{0.4}Mn_{3.6}C$, $Fe_{0.6}Mn_{5.4}C_2$	$MnSiO_3$,$Mn_{22.6}Si_{5.4}C_4$ $(Mn,Fe)_5SiC$	MnO, Mn_2SiO_4, $(Mn,Fe)_{23}C_6$
			Mn_2SiO_4, $(Mn,Fe)_{23}C_6(Mn,Fe)_5SiC$
14	$(Mn,Fe)_7C_3$, $(Mn,Fe)_5C_2$	$Mn_{22.6}Si_{5.4}C_4$ $(Mn,Fe)_5SiC$	Mn_2SiO_4, $MnSiO_3$, $(Mn,Fe)_7C_3$ $(Mn,Fe)_5SiC$
15			Mn_2SiO_4, $(Mn,Fe)_7C_3$, $Mn_{6.4}Fe_{0.6}Si_2$
16			Mn_2SiO_4, $(Mn,Fe)_7C_3$ $(MnFe)_{22.6}Si_{5.4}C_4$
17-19	$(Mn,Fe)_7C_3$		
20			C, $(Mn,Fe)_7C_3$, $Mn_{22.6}Si_{5.4}C_4$
21-30			
		$Mn_{22.6}Si_{5.4}C_4$ $(Mn,Fe)_5Si_3$, C	

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, reducing higher manganese oxides to MnO and iron oxides to metallic iron. In the presence of carbon, hydrogen can also reduce MnO to the metallic manganese. The equilibrium constant for the reaction

$$MnO + H_2 = Mn + H_2O \qquad (7)$$

$$\log K = -7{,}394/T + 1.07$$

calculated using data from Knacke et al. [18], is below 10-3 even at 1500°C (about 10-4 at 1200°C). However, the presence of solid carbon will maintain partial pressure of H_2O at a low level by the reaction:

$$C + H_2O = CO + H_2 \qquad (8)$$

(log K=2.68 at 1200°C and log K = 3.48 at 1500°C), what makes the reduction of manganese oxide by hydrogen in the presence of solid carbon feasible.

Another possible mechanism of carbothermal reduction of manganese oxides in hydrogen atmosphere includes formation of methane as follows:

$$C + 2H_2 = CH_4 \qquad (9)$$

$$MnO + CH_4 = Mn_7C_3 + H_2 + CO \qquad (10)$$

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 unity, 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, what accelerates the overall reduction process.

Higher MnO reduction rate in hydrogen than in helium and in helium than in argon indicates that the reduction rate was mix-controlled by the chemical reaction and internal and external mass transfer.

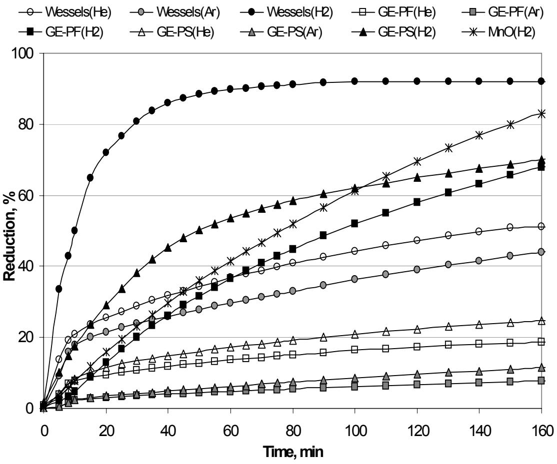

Figure 11: Carbothermal reduction of manganese ores with 30wt% carbon at 1100 °C in hydrogen, helium and argon atmospheres

At high temperature (1400°C), MnO was reduced in hydrogen and in helium with about the same rate, which was higher than in argon. This is an indication, that at 1400°C the reduction rate was controlled by the mass transfer; a role of hydrogen in reduction was insignificant.

Reduction of manganese ores was strongly affected by the ore chemistry. Wessels ore contains much higher iron and calcium oxides and less potassium than both GE ores; while GE-PS has high silica. Wessels ore contained 10.15 wt% Fe, while iron content in GE-PS and GE-PF ores was 5.06 wt% and 3.58 wt% respectively. Iron oxides were easily reduced by hydrogen to metallic iron which acted as nuclei in the reduction of MnO. This can be one of factors explaining faster reduction of Wessels ore in comparison with GE, and higher reduction rate of GE-PS in comparison with GE-PF.

In the reduction of GE ores, manganese silicate was formed, fluxed by alumina and alkali oxides. This silicate was liquid at temperatures above 1100°C. Formation of liquid phase hampered the reduction of GE ores. Wessels ore remains solid at 1200°C; its carbothermal reduction in the solid state in hydrogen atmosphere reached above 90% in less than in 20 min.

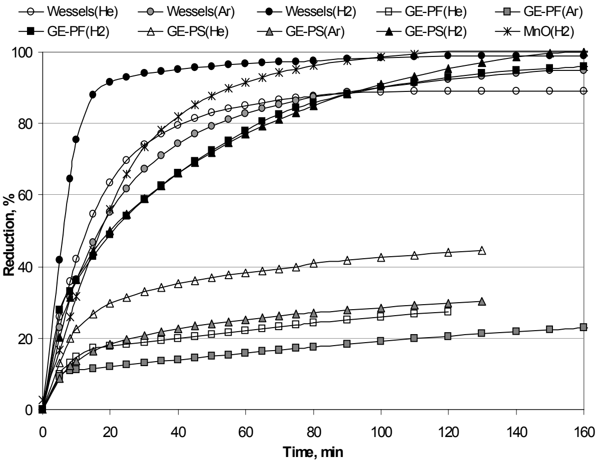

Figure 12:Carbothermal reduction of manganese ores with 30wt% carbon at 1200 °C in hydrogen, helium and argon atmospheres

5. CONCLUSION

Carbothermal reduction of manganese oxide and manganese ores was strongly affected by the reduction temperature and gas atmospheres. Reduction of MnO in hydrogen was close to completion at 1200°C in about two hours, while in helium and argon reduction of MnO was not completed during this reaction time at temperatures below 1300°C. Carbothermal reduction of MnO and manganese ores at constant temperature was the fastest in hydrogen and slowest in argon. Rate and extent of reduction of Wessels ore were higher in comparison with Groote Eylandt ores. Composition of phases formed in the reduction process depended on the manganese oxide to carbon ratio, and was independent of the gas composition. Carbothermal reduction of Wessels ore is feasible in the solid state at 1200 ^{o}C.

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