

Reduction Behavior of Manganese Ore Using Methane Gas

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ABSTRACT

Reduction behaviour of South African Mamatwan manganese ore using methane-argon gas mixture was investigated experimentally in the temperature range of 1000°C to 1200°C. The effect of changing gas mixture composition, time and temperature was studied using a vertical tube furnace. After each test, three representative samples were prepared; one was analyzed by X-ray diffraction to determine the progress of phase changes, chemical analysis were performed on the second sample to obtain metallization results as a function of each reducing condition for each time interval over the total reduction period of two hours. The third sample was mounted, polished and submitted for SEM-EDAX in order to examine the morphology of the ore and its changes in the course of reduction. It was observed that CH₄ was an effective reductant as it cracked, supplying the reaction site with hydrogen gas and very fine solid carbon. The excess carbon from cracking of methane ensures regeneration of reductants CO and H₂ from reaction product gases of CO₂ and H₂O ensuring low partial pressure of oxygen at the reaction site. Hydrogen gas may also be involved in the reduction of iron oxide components of the ore. Moreover, depending upon temperature and CH₄/H₂ ratio in the gas phase the activity of carbon in the system reaches values much higher than unity, shifting the reduction reaction by carbon to lower temperatures. X rays analysis revealed that manganese ore was reduced primarily to carbide Mn₇C₃ at lower temperature range of the experiments, but at 1200°C the dominant reaction product was Mn₅C₂. At higher temperatures extent of reduction was higher reaching over 75% metallization at 1200°C.

Initial results indicate the possibility of rate being controlled by bulk gas mass transfer to the reaction site for initial stage which was then followed by ionic diffusion rate control. Further experimental work is to be conducted using hydrogen-methane gas mixtures with fixed CH₄/H₂ ratios in order to study the reduction process where carbon activity is fixed (at much higher values than one).

1. INTRODUCTION

Manganese is probably the most versatile additive in the steel industry and has the added advantage of low cost and easy availability. Manganese can be added in the form of its ore during iron making or as ferromanganese and silicon manganese in the steel making stage. Various types and grades of ferromanganese and silicon manganese, mostly containing from 70 to 90 percent manganese, are produced in large submerged arc furnaces by carbothermic reduction [1-5]. Operation of the SiMn process is often more difficult than the FeMn process because higher process temperature is needed. A process temperature of 1600 to 1650 °C is necessary to obtain metal with sufficiently high content of Si and discard slag with low MnO. The FeMn slag has a relatively low melting temperature (about 1250 °C). Accordingly, when the Mn ore starts melting at around 1350 °C, it will contain a mixture of solid and liquid phase, where the manganese containing solid phase is MnO. Further heating to 1550 °C or more is necessary before the melting ore will mix with the slag and flow freely and for further reduction. The specific power consumption for production of standard SiMn from a mixture of Mn-ore, high-carbon FeMn smelting slag and Si rich metallic remelts can typically be 3500-4500 kWh/ton of metal, depending on the amount of metallic material added to the feed. Each additional 100 kg of slag produced will consume an additional 50 kWh of electric energy [6-10].

This study is investigating solid state reduction of manganese ore by using methane which is likely to contribute to the lowering of energy use and carbon footprint [11-15]. Most of the reduction to metallic state for both iron and manganese units is expected to take place at solid state reduction temperatures mentioned above which would in principle require only a final melting stage to separate the valuable metallic ferroalloy phase from the slag. Thus, it was essential to conduct kinetic studies on manganese ores to reveal the mechanism of hydrocarbon reduction and establish the rate which determines steps leading to process parameters [16-18].

2. EXPERIMENTAL

The South African Mamatwan ore was used for this study. The composition of the ore is presented in Table 1. The manganese particle size, class of -150 µm + 106 µm was chosen for all the reduction tests.

Table 1. Chemical Composition of Mamatwan manganese ore.

Component	(Mass %)
Mn	37.69
Fe	4.71
SiO ₂	4.51
CaO	16.51
MgO	3.29
Al ₂ O ₃	0.231
P	0.0174.

The reduction experiments were carried out in a molybdenum wound furnace surrounding a thermo gravimetric (TGA) system from bottom. Details of the experimental setup and procedure are available elsewhere [19]. However, due to the chemical decomposition (cracking) of CH₄ gas at about 550°C much lower than the temperatures employed in this work (1000°C –to 1200°C) the TGA could not be used to monitor the reduction reactions. Thus, the progress of the reaction was followed by analytically determining the metallization levels (percentages) of the partially reduced samples at predetermined intervals simply by quenching and removing the samples from furnace. The rest of the experimental procedure was same to those of the previous work conducted in our laboratories [19]. Technical grade argon was used to purge the work tube and acted as a carrier gas for methane. The relative concentration of methane in the argon was changed for different tests. The total gas flow rate was maintained at 880ml/min. Only the manganese and iron oxides were regarded as reducible components of the ore. After each test, three representative samples of the reaction products were split off. One was analyzed by XRD to determine the phase changes. Chemical analyses were performed on the second sample to determine the individual manganese and iron metallization. The third sample was mounted, polished for SEM-EDAX, in order to determine the concentrations (and profile as necessary) of manganese and iron in the individual particles. The experimental variables were time, temperature and concentration of methane in argon.

3.RESULTS AND DISCUSSION

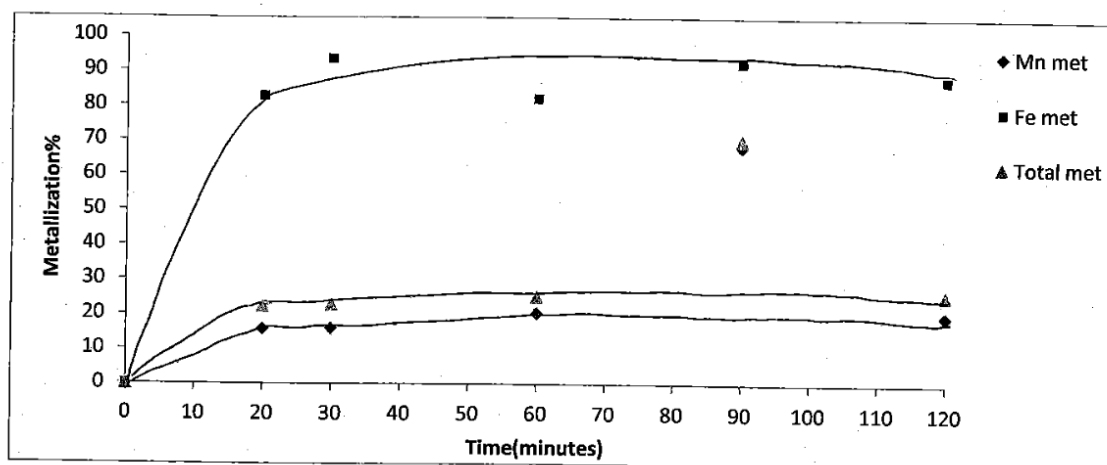
The degree of metallization was calculated using the following equation:

$$\text{Met}_{\text{Mn}} (\%) = (\text{Mn}^0 / \text{Mn}_{\text{Total}}) * 100$$

$$\text{Met}_{\text{Fe}} (\%) = (\text{Fe}^0 / \text{Fe}_{\text{Total}}) * 100$$

$$\text{Met}_{\text{Total}} (\%) = (\text{Mn}^0 + \text{Fe}^0) / (\text{Mn}_{\text{Total}} + \text{Fe}_{\text{Total}}) * 100$$

Where Mn_{Total} and Fe_{Total} represent total Mn and Fe in the product expressed as a percent of the total product mass, Mn⁰ and Fe⁰ represent metallized Mn and Fe in the product expressed as percent of the total product mass, and Met_{Mn}, Met_{Fe}, Met_{Total} represent manganese, iron and total percent metallization respectively.

**Figure 1:** Progress of metallization versus time for tests using 10% CH₄ in Ar at T=1100°C.

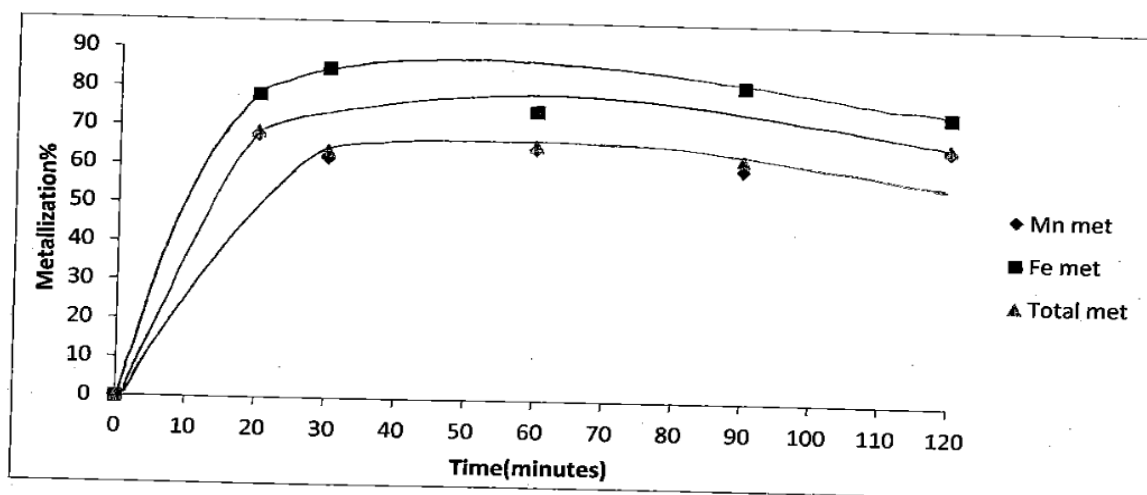


Figure 2: Progress of metallization versus time for tests using 30% CH₄ in Ar at T=1100°C.

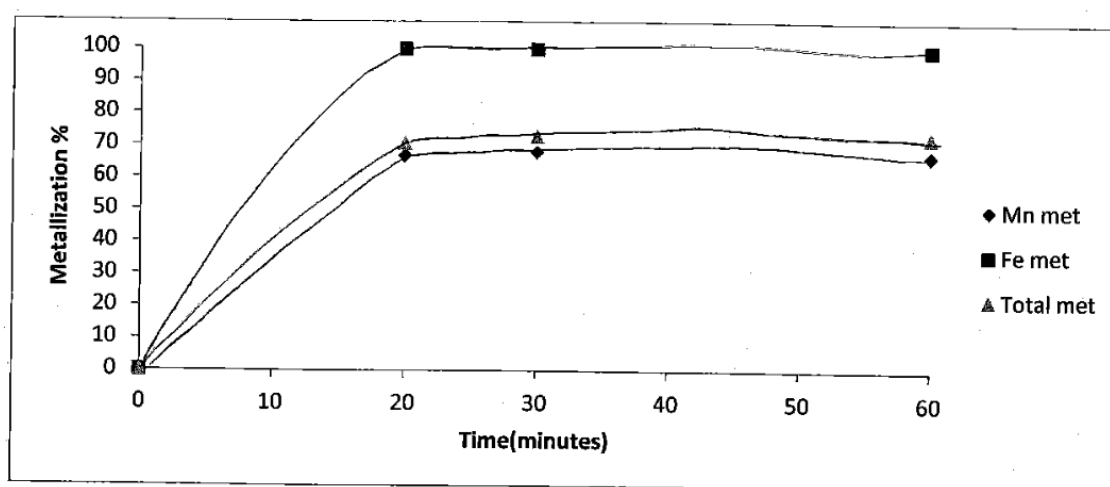


Figure 3: Progress of metallization versus time for tests using 30% CH₄ in Ar at T=1200°C.

Typical plots shown in Figure 1, Figure 2 and Figure 3 illustrate the progress of metallization as a function of time using 10% CH₄ in Ar at 1100°C, 30% CH₄ in Ar at 1100°C and 1200°C. Utilizing such plots, xrd analysis, the results of SEM-EDAX and visual observation the following discussion can be provided on the reduction of manganese using a hydrocarbon gas. In 30% CH₄ in Ar at 1100°C showed that Fe metallization decreased with time after first 30 minutes. This decrease seen on the plots may be due the chemical analysis errors. 1200°C tests using the same gas composition did not reveal such decrease. Further investigation on this issue is in progress.

Total metallization values achieved after two hours ranged from 21% to 72%. The associated Mn/Fe metallization ratios of 0.19 to 0.69 were much higher than those achieved with ordinary solid state carbothermic reduction. The effect of CH₄ concentration and temperature did not have a simple direct relationship with the rate and extent of metallization. The most common occurrence was rapid levelling of reduction rate after first 20 or 30 minutes for all CH₄ concentration and temperatures revealing that the process will take 20 to 30 minutes to complete the reactions which is much quicker than ordinary carbothermic reduction. It was found that higher reduction kinetics would be achieved when using hydrocarbon gas in comparison to classical carbothermic reduction with excess carbon (Burucu ([20]) at a given temperature. At 1100°C reduction achieved by carbothermic reduction with excess carbon was around 35% as reported by Burucu [20], whereas from present work it was noted that metallization reached 70% and above at same temperature of 1100°C.

The XRD analysis revealed that manganese ore was reduced primarily to carbide Mn₇C₃ at lower temperature range of the experiments, but at 1200°C the dominant reaction product was Mn₅C₂.

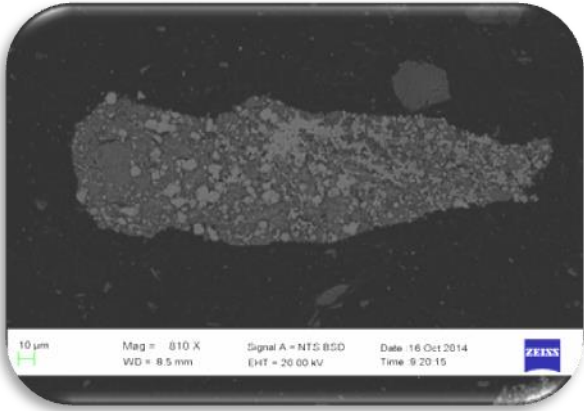
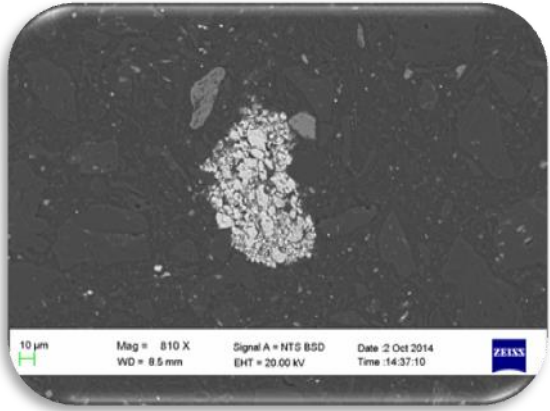
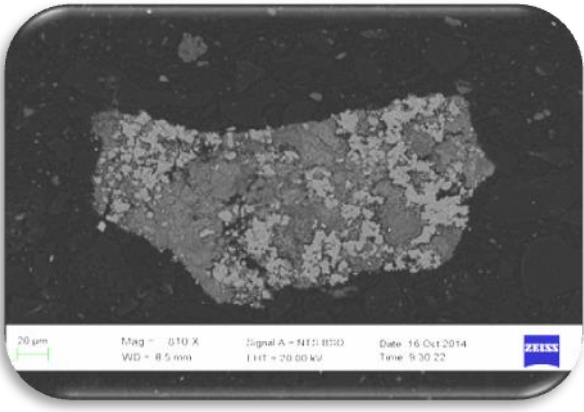
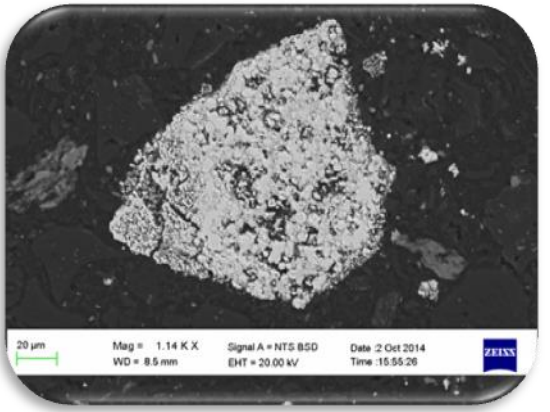
- The oxide feed material analyzed was detected in the form of: CaMn₂O₄
- The following phases appeared under most conditions: Mn₇C₃, Fe₇C₃ and CaMn₂O₄.

- Specifically, with the progress of metallization, the concentration of the original oxide phase decreased with reduction time and a new oxide phase - $\text{Ca}_2\text{FeMnO}_5$ - occurred.
- The Fe_7C_3 appeared as the predominant iron carbide phase early in the reduction test but with progress of metallization, this phase disappeared and was replaced by increasing amounts of Fe_3C .
- Generally, the higher the concentration of methane in the reducing gas, the sooner the Fe_3C appeared potentially due to the higher amount of carbon availability from the decomposition of more CH_4 .
- Manganese ore was reduced primarily to carbide Mn_7C_3 at lower temperature range of the experiments, but at 1200°C the dominant reaction product was Mn_5C_2 .

The extent of reduction required for each phase to appear was dependent on the reaction time and hence on the percent metallization the sample had undergone, and on the reducing gas composition, temperature and hence the amount of carbon deposited.

The particle morphologies were studied mainly by means of photomicrographs of the back-scatter images under SEM as well as results of the energy dispersive analysis of X-rays (EDAX) across particles under different reducing conditions. Figures 4, 5 and 6 compare the resulting particle morphologies using 10% CH_4 in Ar, 20% CH_4 in Ar, 30 % CH_4 in Ar at temperatures 1100°C and 1200°C at times of 20, 30, 60, 90, 120 minutes for 1100°C and 20, 30, 60 minutes for 1200°C . The findings are summarized below:

Changing CH_4 concentration had the effect of changing the kinetic rate and extent of reduction/metallization, and that the CH_4 did not take part directly in the reduction, mainly because it was not stable at these temperatures, cracking around 550°C .

Time	10 % CH_4 in Ar	
	T= 1100°C	T= 1200°C
20 min		
30min		

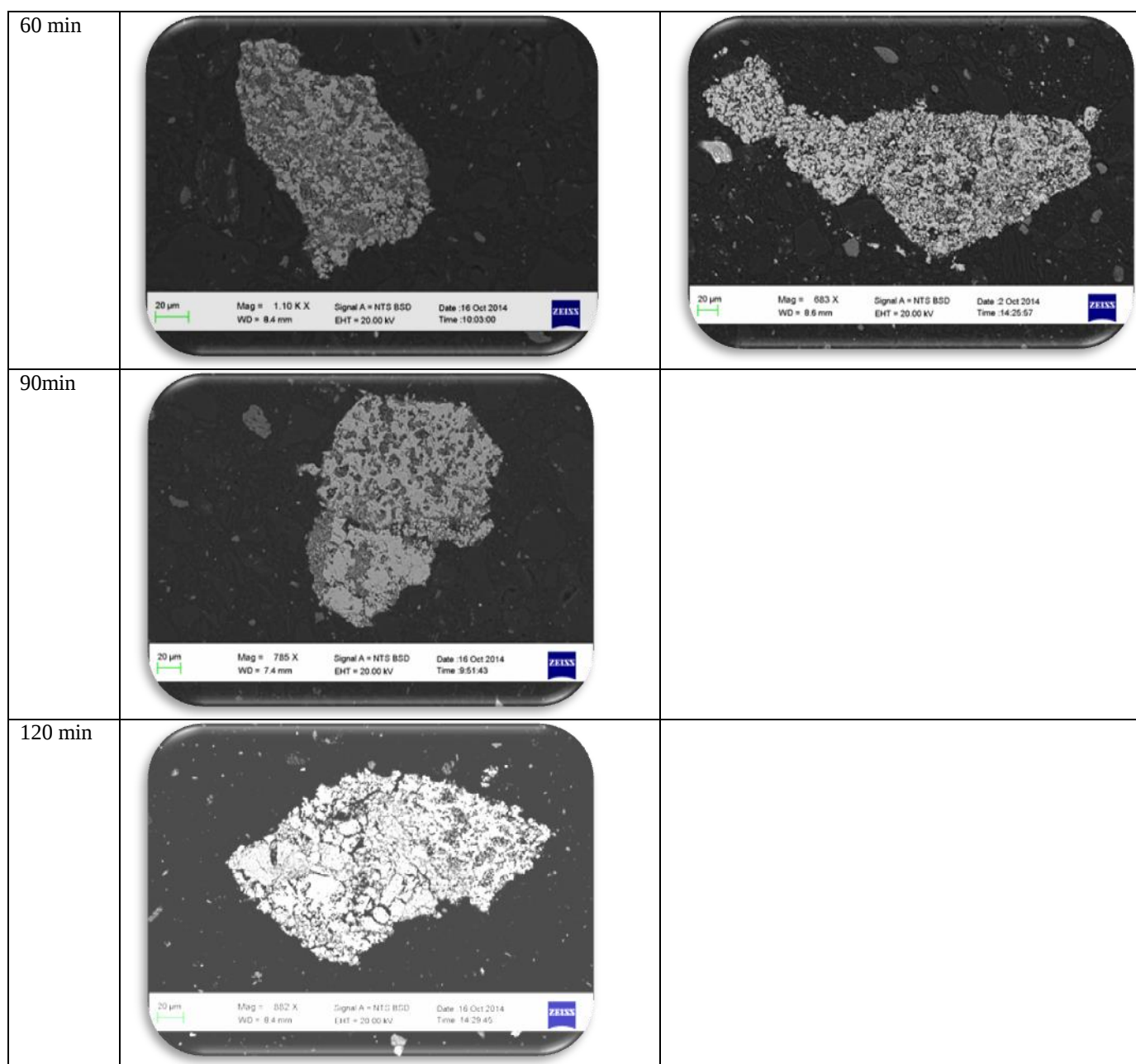
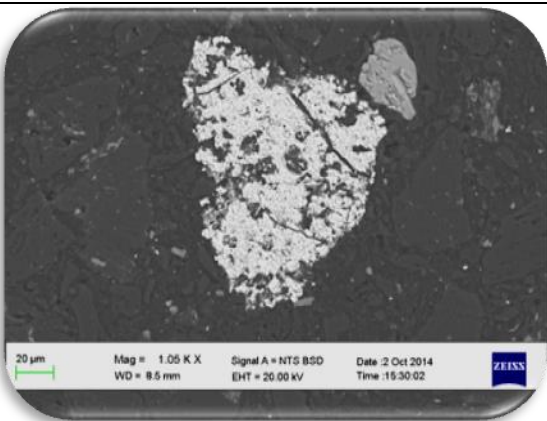
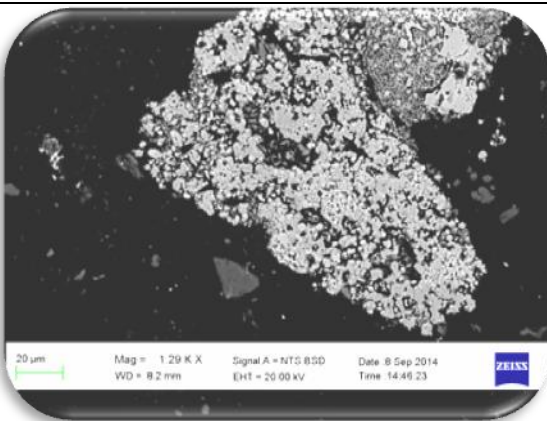
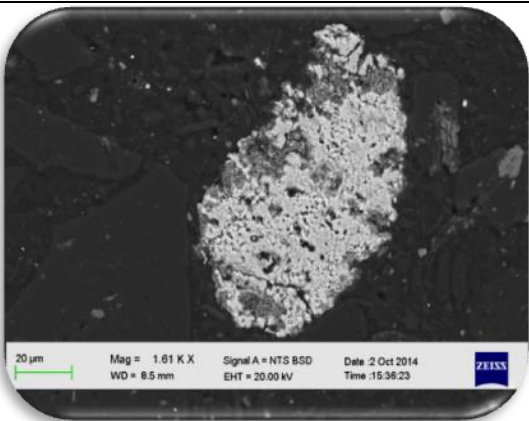
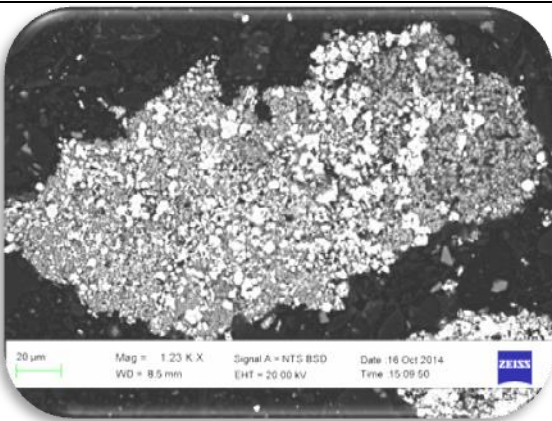
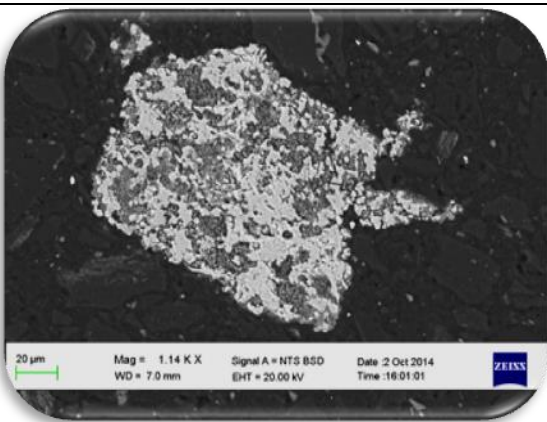
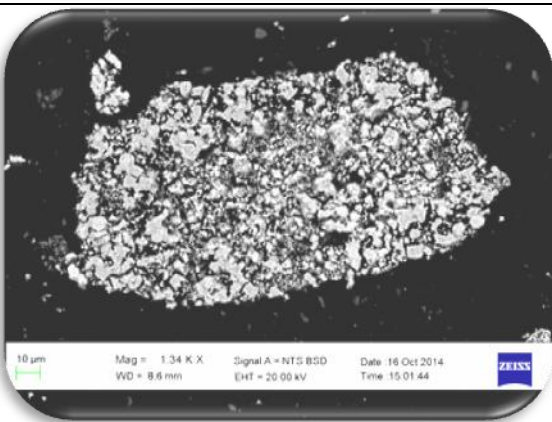
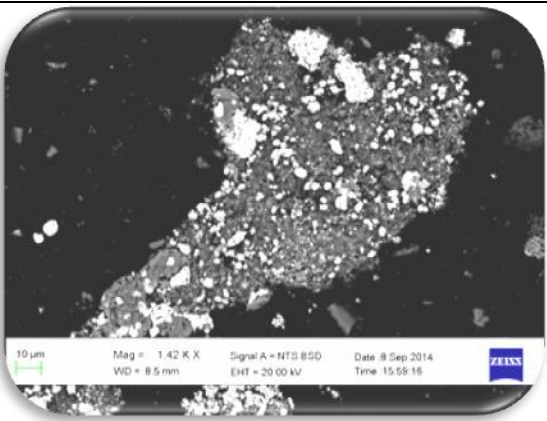


Figure 4: Comparison of particle morphologies using 10% CH₄ in Ar at temperatures 1100°C and 1200°C at periods of 20, 30, 60, 90, 120 minutes for 1100°C and 20, 30, 60 minutes for 1200°C.

Comparison of micrographs in Figure 4 together with metallization data reveal the following at 1100°C: product morphologies of particles reacted under 10% CH₄ in Ar showed that the extent of metallization was around 20-30% for periods below 60 minutes but increased to above 50% for 90 and 120 minutes and at higher temperature of 1200°C the extent of metallization was higher as seen in Figure 4 at 1200°C for the same gas mixture of 10 % CH₄ in Ar.

Time	20 % CH ₄ in Ar	
	T=1100°C	T=1200°C
20 min		
30min		
60 min		
90min		

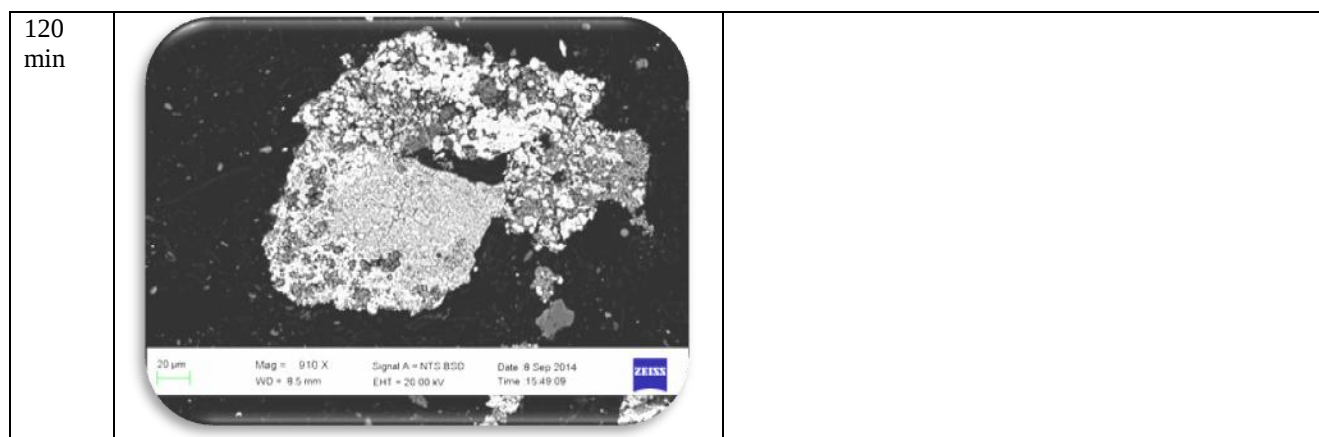
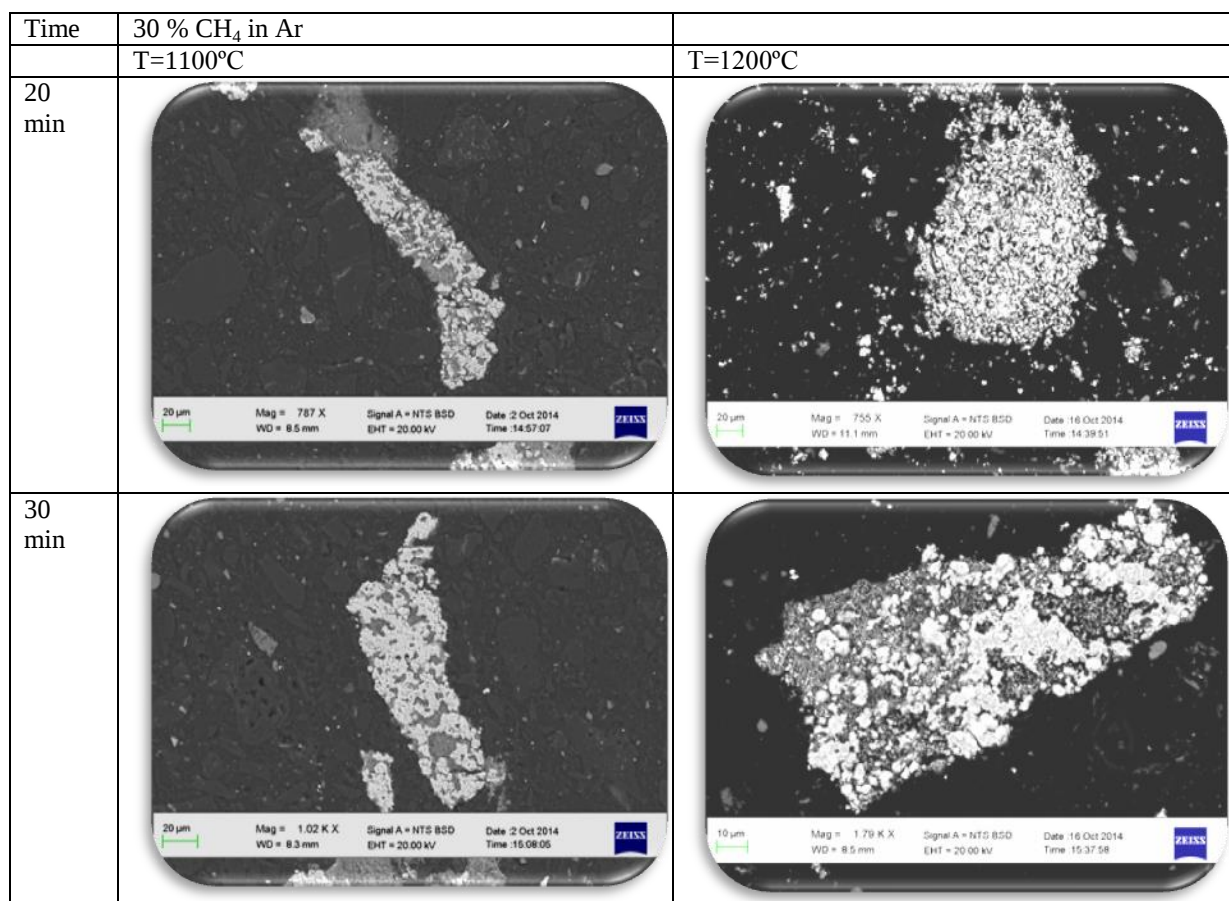


Figure 5: Comparison of particle morphologies using 20 % CH₄ in Ar at temperatures 1100°C and 1200°C at periods of 20, 30, 60, 90, 120 minutes for 1100°C and 20, 30, 60 minutes for 1200°C.

Comparison of micrographs in Figure 5 together with metallization data reveal the following at 1100°C: particles reacted under 20% of CH₄ in Ar showed that the extent of metallization was around 40-50% for periods below 60 minutes but increased to above 50% for 90 and 120 minutes and at 1200°C the extent of metallization was higher.



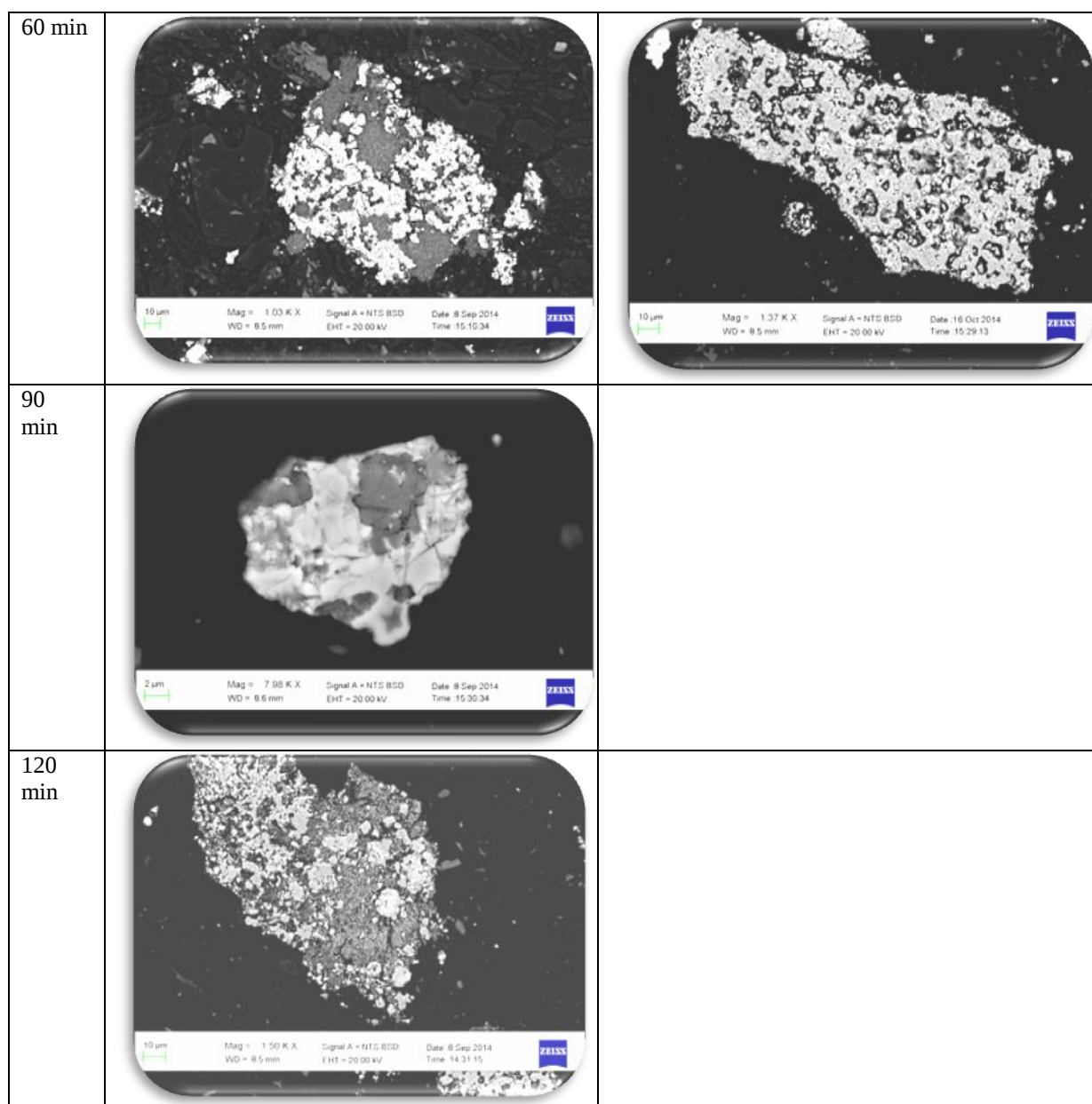


Figure 6: Comparison of particle morphologies using 30% of CH_4 in Ar at temperatures 1100°C and 1200°C at periods of 20, 30, 60, 90, 120 minutes for 1100°C and 20, 30, 60 minutes for 1200°C.

Comparison of micrographs in Figures 6 together with metallization data reveal the following at 1100°C: product morphologies of particles reacted under 30% CH_4 in Ar showed extent of metallization was around 50-60 % for periods below 60 minutes but increased to above 70% for 90 and 120 minute and at 1200°C the extent of metallization was higher over 75% for the same gas mixture of 30% CH_4 in Ar.

Figures 4, 5 and 6 also revealed that the reduction occurred mostly on the particle surface and metallization due to the formation and/or existence of cracks or pores were very limited. It can also be deduced from the micrographs that at higher temperatures the extent of metallization was higher reaching over 75% at 1200°C.

4. CONCLUSIONS

This study explored the use of different concentrations of CH_4 gas in Ar as the reducing gas medium for better understanding of the reduction behaviour of manganese ore at different temperatures. Generally CH_4 was an effective reductant because it supplied both C and H_2 to the reduction site. The reduction sites were limited to the particle surface and there were no significant crack and pore formation. Very fine carbon was formed with thermodynamic activity well above 1.0 due to cracking of CH_4 , that ensured the rapid reaction and regeneration of the reductants CO and H_2 from CO_2 and H_2O was formed as a result of reduction reactions ensuring the maintenance of a high reduction potential even

at lower temperature compared to ordinary carbothermic reduction where maximum carbon activity is 1.0. Manganese ore was reduced primarily to carbide Mn_7C_3 at lower temperature range of the experiments, but at 1200°C the dominant reaction product was Mn_5C_2 . The higher the concentration of the methane in the gasphase, the higher the resulting reaction rate and extent. It can be also deduced that at higher temperatures the extent of metallization was higher reaching over 75% at 1200°C.

5. ACKNOWLEDGEMENT

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6. REFERENCES

- [1] Antonov, V. K and Chufarov, G. I. "Reduction of MnO by solid carbon". Tr. Inst. Met. akad. Nauk SSSR, Uralsk. filial, 7, 1961, pp. 101-105.
- [2] De Villiers, J.P.R. "A mineralogical investigation of natural and heated Mamatwan manganese ore". Johannesburg. NIM, technical memorandum, no.1, 1973, 12pp.
- [3] Hahn, W. C and Muan, A. "Studies in system Mn-O. The Mn_2O_3 - Mn_3O_4 and MnO equilibria", Am. J. Sci, vol.258 (1), 1960, pp. 66-78.
- [4] Jones, R, and Meichack, K. "Thermo. Software for thermodynamic calculations", Council for Mineral Technology, Pyrometallurgy Division, 1990.
- [5] McRae, B. L "The Pre-reduction of Mamatwan-type ores". NIM. Report - no 2020, 1981, 11pp.
- [6] Pentz, R. D . Msc. Dissertation, Potchefstroom University, 1970.
- [7] Pilter, P. "The Reduction of metallic oxides with solid carbon", Kohasz.lapok, vol.100, 1967, pp.303-308.
- [8] Pilter, P. "The reduction of manganese oxides in solid state with carbon monoxides and hydrogen". kohasz.lapok, vol.100, 1967, pp. 492-500.
- [9] Rao, Y. K. Met. Trans, vol.2B, 1971, pp. 1439-1447.
- [10] Samancor. Brochure describing the manganese and iron ore interests of the Samancor Group of companies, Samancor, Johannesburg, 1979.
- [11] Ostrovski, O, Anacleto, N., and Ganguly, S. "Reduction of manganese ores by methane containing gas" Proceedings: Tenth International Ferroalloys Congress; 1 - 4 February INFACON X, 2004, pp. 173-183, Cape Town, South Africa.
- [12] Ostrovski, O. and Zang, G. "Reduction and carburization of metal oxides by methane containing gas", AICHE, Journal, 52, 2006, pp. 300-310.
- [13] Kononov, R., Ostrovski, O. and Ganguly, S. "Carbothermal reduction of manganese oxide in different gas atmosphere", Metallurgical and Materials Transactions B, 39B, 2008, pp. 662-668.
- [14] Kononov, R., Ostrovski, O and Ganguly, S. "Carbothermal solid state reduction of manganese ores: 1". Manganese ore characterisation, ISIJ International, 49(8), 2009, pp. 1099-1106.
- [15] Kononov, R., Ostrovski, O. and Ganguly, S. "Carbothermal solid state reduction of manganese ores: 3". Phase Development, ISIJ International, 49(8), 2009, pp. 1115-1122.
- [16] Oslen, S. E., Tangstad, M. and Lindstad, T. "Production of manganese alloys", 2007, pp. 43-110, Sintef and Tapir Academic Press, Trondheim.
- [17] Turkdogan, E. T. Physical chemistry of high temperature Technology, Academic Press, N.Y, 1980.
- [18] Oslen, S. E., Tangstad, M. "Silico-Manganese production process understanding", Tenth Ferro-Alloy Congress, INFACON X, 2004, pp. 231-238, Cape Town, South Africa.
- [19] Akdogan, G. "Kinetics and mechanism of the solid state carbothermic reduction of wessel type ferromanganese ores". PhD thesis, University of Witwatersrand, Johannesburg, 1992.
- [20] Burucu, E. "Kinetics and mechanism of the reduction of mamtwan manganese ore fines by solid carbon". M.Sc thesis, University of Witwatersrand, Johannesburg, 1991.