

COMPARATIVE STUDY OF PHASES FORMED DURING HCFEMN UNDER CO AND CARBON: PREREDUCTION

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Abstract

During High Carbon Ferromanganese production, the understanding of phases formation is of vital importance since they determine the quality of the overall operations in the furnace. This is also strongly dependent on the chemical composition of the feed. As opposed to other manganese ores that are acidic, South Africa has a basic manganese ore. The formation of phases during HCFemn from still needs more investigation since it has been found that some theories do not explain what is observed in the South African manganese industry. The current work compared the phases that formed in the prerelution zone when carbon was used as opposed to carbon monoxide being blown into the furnace. Manganese ore from Nchwaning was used in the current work. Coke containing 86 % fixed carbon and a bottle containing CO with 98 % purity were used. The basicity was adjusted to 1 through addition of silica. The ore and the flux were crushed and milled together for better homogenization of the feed. XRD, XRF and SEM were used to characterize the feed and the products. The working temperatures were from 1200°C to 1300°C with 50°C increment. Graphite crucible was used for the experiments. To ensure that products analysed were not from the interaction with the crucible, only samples from the centre of the crucible were considered. Experiments were conducted in an alumina tube furnace for two hours after reaching the aimed temperature. Although carbon monoxide was blown into the furnace at a rate to ensure more reducing conditions that would presumably prevail same than when using carbon, results show similarities in the phase composition but the MnO content differed considerably.

Keywords: Ferromanganese, Prerelution, phases comparison

1. INTRODUCTION

The production of High carbon ferromanganese requires a vast amount of data to understand different mechanisms during operations in the furnace. Generally speaking, the quality of products is dependent on the feed [1-3]. A better quality of products must be achieved on one hand and the energy consumption must be monitored on the other hand. Both have been reported to be directly dependent on the quality of the manganese ore [4-8]. Investigations have also shown that the degree of prerelution could be as high as 60 % and that the chemical composition of the manganese ore had a remarkable on the degree of prerelution [9]. The rate of MnO reduction from a slag of high carbon ferromanganese was investigated. It was found that graphite that was used for reduction had an effect and depended on the properties of the graphite [10]. Another study conducted on the reduction kinetics of manganese oxide has shown that carbon monoxide gave a higher reduction rate than argon although the expectation was that argon should have provided a high driving force [11]. The same study showed that charcoal gave a higher rate of reduction as opposed to coke. The above gave an indication that different atmospheres created by different reductants or different sources of carbon played an important role. Investigations on the kinetics of a number of manganese oxides ores have revealed that the temperature and the nature of the ore determined the degree of reduction [12]. The correlation between time and percentage reduction was found to be directly proportional [13]. The medium of reduction as well as the crucible used have been found to have an impact on the reduction rate of MnO [14-17]. Early investigations of reduction of pyrolusite in the temperature range of 250- 450°C under CO gas have revealed that the reduction went through Mn₃O₄ down to MnO [18]. The current investigation focused on comparing the reduction

of manganese ore using CO gas and in presence of coke. Based on different works conducted previously on different manganese ores that were acidic, the current investigation looked at a basic manganese ore from South Africa and the impact of the type of reductant on the quality of the products obtained. Since South Africa has the 70 % world reserves of manganese, but only contribute with 30 % of the world production, it was imperative that thorough investigations be conducted in order to improve the productivity [19].

2. EXPERIMENTAL PROCEDURE

Materials

In this work, a basic manganese ores from South Africa were used for the investigation. Silica was used as flux. Graphite crucible, silica crucible used to hold the graphite crucible to avoid spillages if it so happened. A bottle of carbon monoxide provided by Afrox was used for reduction. A vertical alumina tube furnace heating at a rate of 7°C/ min was used in this investigation. XRF, XRD and SEM-EDS were used for characterization of the feed and the products.

Methodology

For the first type of experiments, the ore was mixed with the required amount of fluxing agent and milled together for 15 minutes to homogenize the sample. For the second type of experiments, the ores was mixed with the flux and coke were milled together for 15 minutes to homogenize the head sample. After homogenization, the head sample was placed in a graphite crucible which in turn was placed in the hot zone of the tube furnace. The experiments were conducted at 1200°C. After reaching the set temperature, the sample was kept in the furnace for two hours then the furnace was switched off to cool down to room temperature. The feed and the products were analyzed using XRF, XRD and SEM.

3. RESULTS AND DISCUSSION

Figure 1 below provides the XRD results of the manganese ore used in the current investigation. The same samples were used in previous investigations conducted by same authors. It was observed that the manganese ore was essentially composed of braunite, hausmannite, bixbyte, hematite, quartz and calcium iron silicate.

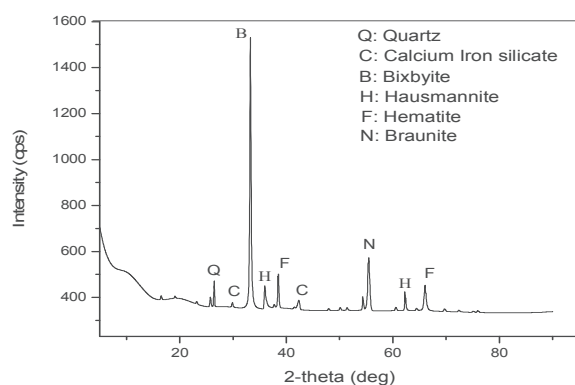


Figure 1 XRD results of the manganese ore [19]

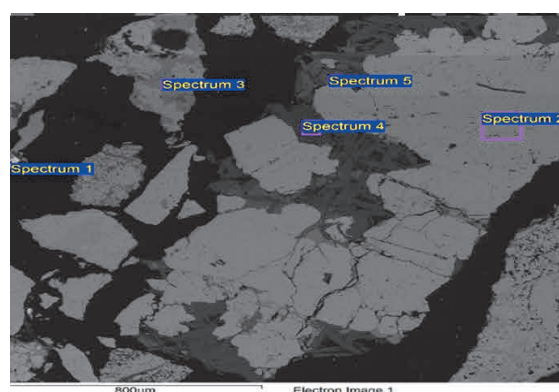


Figure 2 SEM of the manganese ore [20]

Table 1 provides the results obtained with SEM-EDS on the chemical composition of the ore as per micrograph presented in **Figure 2** above.

Table 1 Analysis of the spectra in **Figure 2** [20]

Spectrum	Mn	Fe	Al	Si	Ca	Mg	Phases	Formulas
1	6.7	-	-	-	1.05	-	Braunite	Mn.Mn ₆ (SiO ₄)O ₈
2	56.27	11.13	-	4.07	4.01	-	Bixnyte	(Fe,Mn) ₂ O ₃
3	1.21	15.43	1.21	20.75	22.82	-	Hausmannite	(Mn ₃ Fe)O ₄
4	0.46	0.57	9.87	18.25	-	24.71	Calcium iron silicate	CaFeSi ₂ O ₆
5	1.1	-	2.34	3.34	53.66	7.18	Quartz	SiO ₂

The observations made from **Table 1** were that the SEM-EDS results were in line with the chemical composition of the ore obtained with XRD spectrum in **Figure 2**. The presence of braunite, bixbyte, hausmanite calcium silicate and quartz was confirmed. The above results were for the same samples used in previous studies conducted by same authors.

Table 2 XRF analysis of the manganese ore [20]

Oxide	MgO	Al ₂ O ₃	SiO ₂	CaO	MnO ₂	Fe ₂ O ₃	Basicity	Mn/Fe
Mass (%)	1.03	0.93	4.89	5.29	66.85	19.56	1.1	
Element	Mg	Al	Si	Ca	Mn	Fe		3.1
Mass (%)	0.97	0.77	3.56	5.89	65.80	21.31		

The CO gas was provided by Afrox and contained 99.06 % carbon monoxide while the analysis of the coke used in this investigation was provided in **Table 3** below.

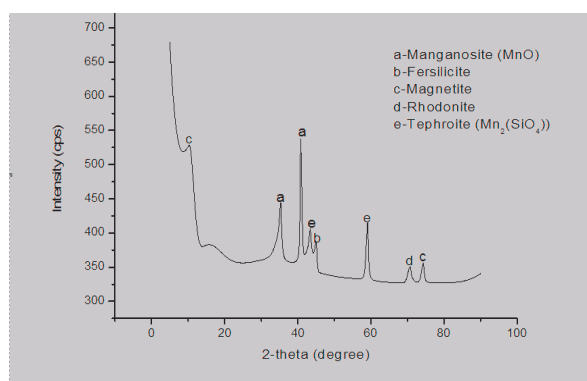
Table 3 Proximate and ultimate analysis of the reductant

Parameter	Proximate analysis (AR)			
	Fixed-C	Volatile	Ash	Moisture
Coke	83	3.9	11.7	1.8

AR: As Received, Fixed carbon by difference [100 - (Volatile matter + Moisture + Ash content)]

From **Table 3**, it could be seen that carbon fixed is 83 %, volatile matters are 3.9 % whereas ash content amounts to 11.7 % and moisture 1.8 %. This indicated that the coke used is not of low quality.

The XRD results of products obtained with coke as reductant are provided in **Figure 3** below.


Figure 3 XRD pattern of products obtained at 1200 °C in presence of coke

From **Figure 3**, following phases have been identified: rhodonite, silica, iron, tephroite, fayalite manganooan and hausmanite. This indicated that some iron oxides were already reduced to iron while hausmanite was still present in the products. However, tephroite formed as well as rhodonite and slag started to form.

Figure 4 below gives the SEM results of the products obtained at 1200°C in presence of coke.

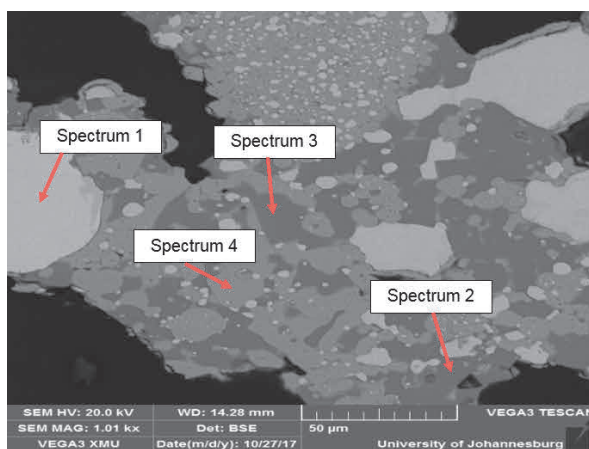


Figure 4 SEM micrograph of the sample reduced at 1200 °C with coke

Table 4 EDS analysis results of the sample reduced at 1200 °C with coke

Spectrum	Weight (%)								Phases
	F	Mg	Al	Si	Ca	Mn	Fe	O	
1						41.34	58.66		FeMn
2	3.24			15.8	15.5	30.42	0.48	33.73	Rhodonite (MnSiO ₃)
3	3.79	0.72		11.5	11.0	40.00	2.66	30.35	Tephroite (Mn ₂ SiO ₄)
4	5.71	0.57	0.38	0.40	0.58	68.38	1.32	21.79	Manganosite (MnO)

The SEM-EDS results shown in **Table 4** confirmed the phases identified with XRD in **Figure 4**. These phases were namely rhodonite, tephroite and MnO as well as iron. However, it was observed from the XRD that magnetite was also present. Further, ferromanganese alloy formed at this stage. This was an indication that reduction conditions were strong enough to get part of the ore being reduced down to the alloy. Therefore, it could be assumed that lower oxides of manganese and iron were reduced to obtain the alloy. This was also observed in previous works [7]. But most probably due to its very small amount, the alloy was not detected this was not detected with XRD. It implied that the amount of alloy that formed was very low.

The **Figure 5** below provides the XRD pattern of products obtained with the use of carbon monoxide gas only.

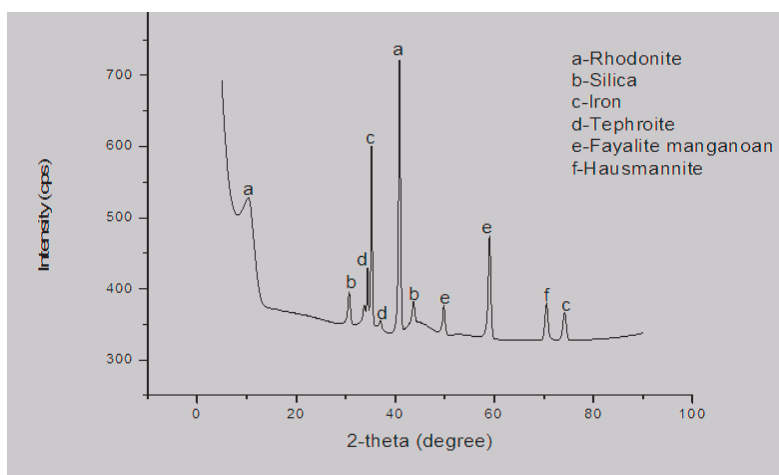


Figure 5 XRD pattern of products obtained at 1200°C with the use of carbon monoxide gas only

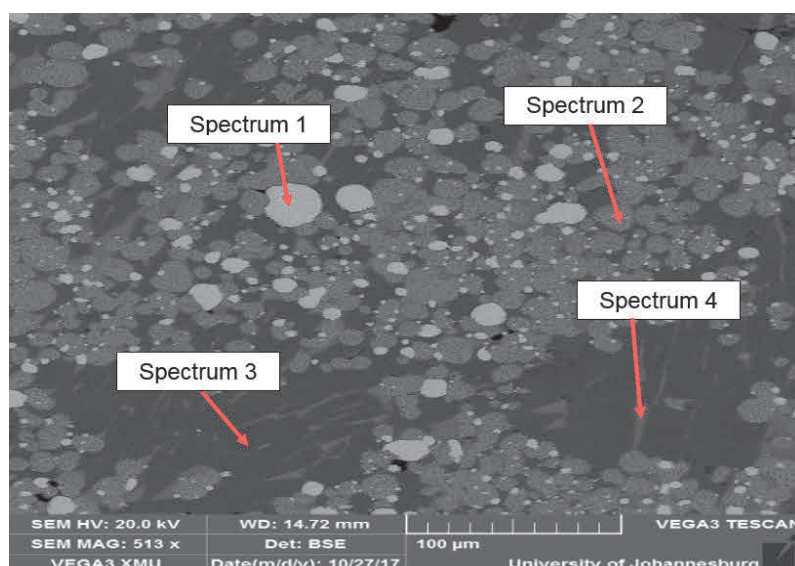


Figure 6 SEM micrograph of the sample reduced at 1200 °C with carbon monoxide gas only

Table 5 SEM-EDS analysis results of the sample reduced at 1200 °C with carbon monoxide gas only

Spectrum	Weight (%)								Metal/Phases
	F	Mg	Al	Si	Ca	Mn	Fe	O	
1						54.48	46.39		FeMn
2	5.67	1.02		2.35	2.13	60.26	5.31	23.27	Manganosite (MnO)
3	3.39	0.89		17.2	15.7	28.16		34.66	Tephroite (Mn ₂ SiO ₄)
4	3.19	0.93	0.33	16.6	16.1	28.32		34.51	Rhodonite (MnSiO ₃)

From **Table 5**, it can be observed that manganosite, tephroite, rhodonite are present in the products. These phases are same that were present in the micrograph of products obtained with coke except magnetite. Also, same as observed with the use of coke, no ferromanganese was detected with the XRD, but identified with the SEM. However, from visual analysis, it was observed that the size of FeMn was bigger when coke was used as reductant than when carbon monoxide was blown in the furnace without coke presence. This led to an observation that, when carbon monoxide was blown into the furnace, the residence time might have been short such that it did not have enough time to reduce the ore. Although measurements were not taken to quantify the amount of reducing gas in the furnace for the two types of atmospheres, it can however be observed that in the prereduction zone only the degree of reduction differed since with coke magnetite also appeared in the products.

4. CONCLUSION

The current investigation on the influence of coke compared to carbon monoxide used at the same temperature to reduce a manganese oxide ore in the prereduction zone have revealed that:

- 1) The phases that formed were very much similar. Although the XRD was not able to detect the alloy that formed while SEM results have confirmed the presence of FeMn. This was an indication that although the temperature was relatively low, there was a considerable reduction for the lower oxides of manganese and iron to have the manganese alloy occurring so early.
- 2) The size of FeMn metal was bigger when coke was used as reductant than when carbon monoxide was blown in the furnace without coke presence. This implied that, when carbon monoxide was blown into

the furnace, the residence time might have been short such that it did not have enough time to reduce the ore as compared to coke.

- 3) Although measurements were not taken to quantify the amount of reducing gas in the furnace for the two types of atmospheres, it can however be observed that in the prereduction zone only the degree of reduction differed since with coke magnetite also appeared in the products.

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