

STUDY ON THE INFLUENCE OF Al_2O_3/SiO_2 ON THE KINETICS IN THE PREREDUCTION ZONE DURING HIGH CARBON FERROMANGANESE PRODUCTION USING BASIC SOUTH AFRICAN MANGANESE ORES

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Abstract

During the production of high carbon ferromanganese, the feed undergoes different stages of reduction. Three main zones were assumed instead of traditional four. The influence of phases formed during pre-reduction have a gigantic impact on the kinetics of the quality of the final products. In the current investigation, basic South African manganese ores were used. Two different fluxes were tested namely alumina and silica. For the experiments the ore, flux and coke were mixed and milled to 75 μm for 15 minutes for better homogenization. Using a graphite crucible placed into a silica crucible, the crucible was placed in the hot zone of the alumina tube furnace which was programmed at different temperatures. To avoid the reaction between the graphite crucible and the manganese ore. Argon was blown into the furnace from room temperature to 600 °C then switched off to allow carbon only to react with the oxide ore. The furnace was kept for two hours and switched off until the furnace reached 600 °C then argon was blown into the furnace down to room temperature. XRD, XRF and SEM were used for characterization. With the use of alumina as fluxing agent the temperatures used were 1200, 1250 and 1300 °C whereas with silica used as fluxing the temperatures tested were 1200 and 1350 °C. The influence of the A/S (alumina/silica) ratio on the kinetics was assessed.

Keywords: Metallurgy, Al_2O_3/SiO_2 , kinetics, pre-reduction, South African basic manganese ores

1. INTRODUCTION

Kinetics in the production of high carbon ferromanganese (HCFMn) are key in the performance of the process and the quality of the products. Based on the reactive zones that have been identified by different researchers [1-4], it transpired that the reactivity of each zone needs a thorough investigation for a better process. Using Mamatwan manganese ore fines, the mechanism and kinetics of the carbothermic reduction was investigated [5]. Separate pre-reduction unit was found to be advantageous in saving energy, having stable operations and better control of carbon balance [6]. The effect of SiO_2 addition on the reduction rate was conducted and found to be considerably influential on the slag formation [7]. Silicates liquid phase was depicted during carbothermic reduction at 1200 °C using Wessels ore [8]. Higher basicity was found to be decreasing the reduction rate [9]. Although a number of investigations have been conducted, due to the behaviour associated with the chemical composition of the raw material, it remains important to investigate the rate of reduction depending on the fluxes that are used to adjust the basicity. The current investigation aimed at studying the influence of Al_2O_3/SiO_2 ration on the kinetics using a basic South African manganese ore, using alumina and silica as fluxing agent.

2. EXPERIMENTAL

2.1. Materials

The manganese ore used in this investigation is a basic South African ore from Nchwaning. Two fluxes namely alumina and silica were used to decrease the basicity down to one. The fluxes were provided by the Department of Metallurgy, University of Johannesburg. Argon and carbon monoxide cylinders provided by Afrox Africa.

2.2. Equipment and methodology

An alumina tube furnace with a heating rate of 7 °C/min, graphite crucible were used for the experiments. XRD coupled with Topaz and Rietveld, XRF, SEM-EDS were used for characterization of the feed and products.

The ore was mixed with the stoichiometric amount of coke, the required amount of flux to adjust the basicity to 1. The mixture was milled together for 15 minutes to enhance homogenization of the feed. The feed was placed in a graphite crucible which in turn was placed in the hot zone of the furnace. Argon was blown in the furnace from room temperature to 600 °C and the valve was switched-off until the aimed temperature was reached. The sample was kept for two hours at the aimed temperature and the furnace was switched-off and the argon valve open as soon as the furnace temperature reached 600 °C till room temperature. The products were collected and analysed.

3. RESULTS AND DISCUSSION

The XRD results of the ore used in this investigation are presented in **Table 1** below.

Table 1 Mineralogical analysis of the manganese ore

Mineral	(wt%)	Mineral	(wt%)
Braunite 1 $Mn^{2+}Mn^{3+}_6O_8SiO_4$	44	Hematite Fe_2O_3	9.6
Braunite 2 $Ca(Mn,Fe)_{143}SiO_{24}$	25	Barite $BaSO_4$	1.0
Bixbyite $Mn^{3+}_2O_3$	7	Calcite $CaCO_3$	9.4
Hausmannite	1.8	Manganite $MnO(OH)$	1.7

The mineralogical results revealed that no pyrolusite, kutnohorite, jacobsite and wollastonite were present in the sample. The most predominant manganese minerals are braunite 1 which is the most abundant followed by braunite 2 while bixbyite and hausmannite are in a low amount. The iron mineral is essentially hematite.

3.1. Influence of temperature and alumina on the kinetics

The temperature ranged from 1200 °C to 1300 °C. **Figure 1** below depicts phases during the carbothermic reduction at 1200 °C (a), 1250 °C (b) and 1300 °C (c).

In the samples from the experiment with alumina addition at 1200 °C, there is coexistence of a MnO solid phase with a liquid since the sample had sintered. The presence of MnO (manganosite) confirms that Mn_2O_3 reduction has rapidly progressed down to MnO as discussed earlier. This confirms that the rapid reduction stage occurs during pre-reduction. The rapid reduction stage still does not depend on the basicity.

The addition of alumina has slightly diluted the SiO_2 fraction which favours more the formation of Mn_2SiO_4 . The presence of Mn_2SiO_4 in the sample indicates the substitution of some of the MnO by SiO_2 .

The reduction rate of FeO was found to decrease with silica addition and that silica interfered with the second stage of FeO reduction [10]. The reduction rate of MnO is rapid when MnO at solid state, this being due to the

high and constant activity of MnO. At this stage, since there is coexistence of solid and liquid MnO, the relative proximity of the phases to one another and reduction interface place do not remain at the same place.

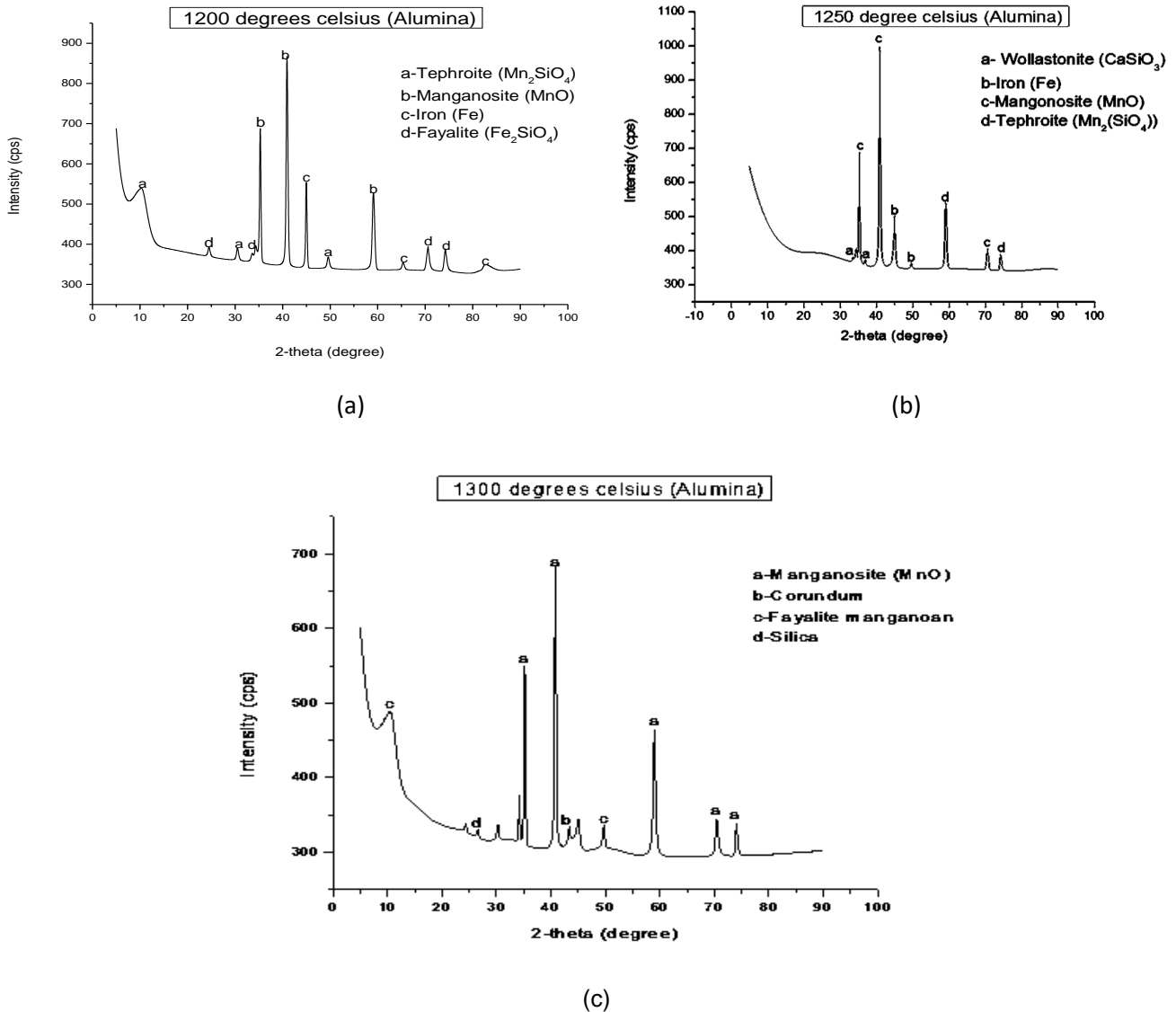


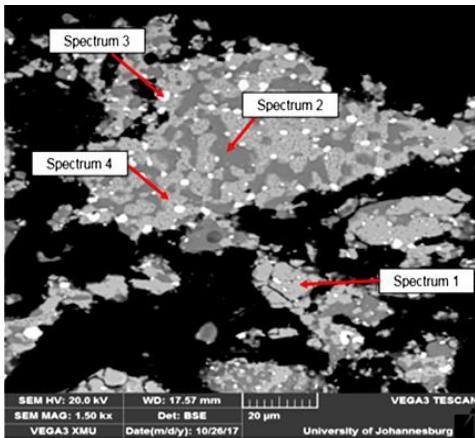
Figure 1 XRD spectrums with alumina addition

The addition of acidic fluxes to lower the basicity leads to high MnO in the liquid phase than the solid phase since the fluxes added substitute MnO. The composition of the liquid phase is temperature dependent not essentially on the progression of the reduction. On the other hand, the reduction of iron has progressed down to metallic iron.

The microscopic results for the samples produced at 1200 °C, 1250 °C and 1300 °C with alumina addition are presented respectively in **Figures 2 (a), (b) and (c)** below.

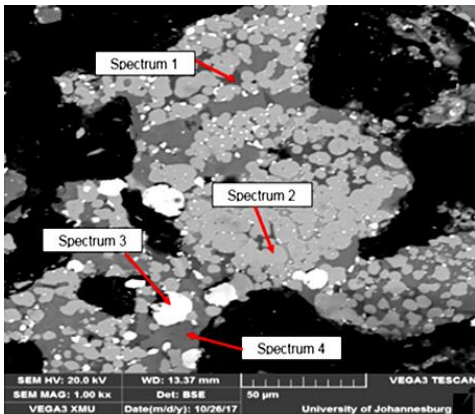
The SEM-EDS results confirmed all the phases that were depicted with XRD. However, the SEM revealed that the metallic iron nuclei alloyed with manganese.

The coexistence of liquid and solid phase is confirmed with more liquid formed. From the **Figure 2**, it is observed that the majority of phases depicted at 1200 °C remain at 1250 °C.



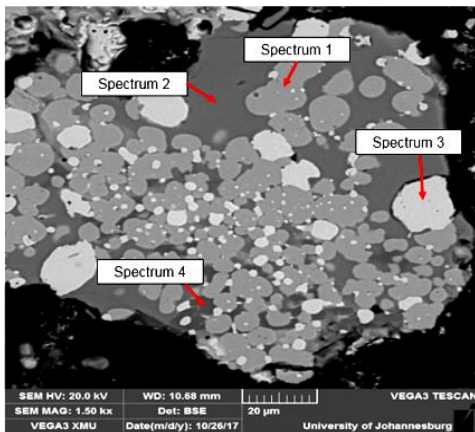
Spectrum	F	Mg	Al	Si	Ca	Mn	Fe	O	Metal phases
1	7.73	0.68			0.29	59.66	10.65	20.99	Manganosite (MnO)
2	4.55	0.8		11.8	12.3	32.82	6.22	30.64	Tephroite (Mn ₂ SiO ₄)
3						14.27	85.73		Metal (FeMn alloy)
4		0.24	1.70	2.02	3.16	9.86	58.23	24.79	Fayalite (Fe ₂ SiO ₄)

(a)



Spectrum	F	Mg	Al	Si	Ca	Mn	Fe	O	Metal phases
1		0.15	14.5	11.1	26.2	5.55	0.26	38.6	Wollastonite (CaSiO ₃)
2	4	0.7	0.4			73.01		21.89	Manganosite (MnO)
3						21.47	78.56		Metal (FeMn alloy)
4	3.36	0.77	0.03	15.4	19.4	26.86	0.4	33.78	Tephroite (Mn ₂ SiO ₄)

(b)



Spectrum	F	Mg	Al	Si	Ca	Mn	Fe	O	Metal phases
1		0.81			0.66	74.93	0.76	22.84	Manganosite (MnO)
2	1.82	0.9		15.3	3.68	27.21	21.5	34.18	Fayalite manganooan
3						42.38	57.62		Metal (FeMn alloy)
4		0.22	16.6	11.2	25.5	3.11	0.41	39.54	Corundum (Al ₂ O ₃)

(c)

Figure 2 SEM micrographs with alumina addition

However, it should be noted that in addition to other phases CaSiO₃ (wollastonite) has formed. Manganosite (MnO) is still present. Metallic iron at solid-state and tephroite are present. Once again, this indicates the substitution of some MnO by SiO₂. Fayalite has however disappeared and decomposed into silica and wustite. The later was reduced and iron reported to metallic iron while silica contributed toward the formation of wollastonite. This implies that calcium silicide is more stable than fayalite at this range of temperature. It is therefore crucial to note that the formation of silicate phases is predominant. It is observed that the Mn content increased. This implies that more Mn dissolved into the alloy.

At 1300 °C however, the dissolution of FeO in alumina is observed through the appearance of corundum in the sample. Manganosite (MnO): As the previous two temperatures, MnO is still present. However, at this

temperature more manganese is expected to diffuse and dissolve into the alloy. This is supported with the SEM-EDS results. There is very little about manganese formation metallurgically obtained. This is due to manganese oxide and iron oxide have reacted with silica to produce a double silicate of iron and manganese. This contributed toward reducing the rate of reduction of MnO and allowing the silicates to build barriers around MnO. However, the alloy composition shows an increase in manganese content. This is in line with the expectations since the temperature has increased and that the activity of MnO in the forming slag has decreased. The activity could have been higher since the formation of silicates have prevented some of the MnO to remain active. At this stage, it could be assumed that the progression is toward the decrease in MnO. This implies that the rapid reduction stage is heading to its end, lower MnO activity and the MnO have started dissolving into the liquid slag. The fast reduction is therefore expected to stop as the temperature increases from the current value. This is confirmed with the presence of fayalite manganese which can hinder the reduction process. It can therefore be stated that during carbothermic reduction in the production of high carbon ferromanganese, the activity of MnO is dictated by stage of reduction.

3.2. Influence of temperature and silica on the kinetics

As opposed to alumina addition the A/S ratio has decreased since silica has increased. This has an implication on the ionic structure of the slag. The XRD results on the influence of silica addition as fluxing agent at 1200 °C and 1350 °C are presented in **Figures 3 (a) and (b)**.

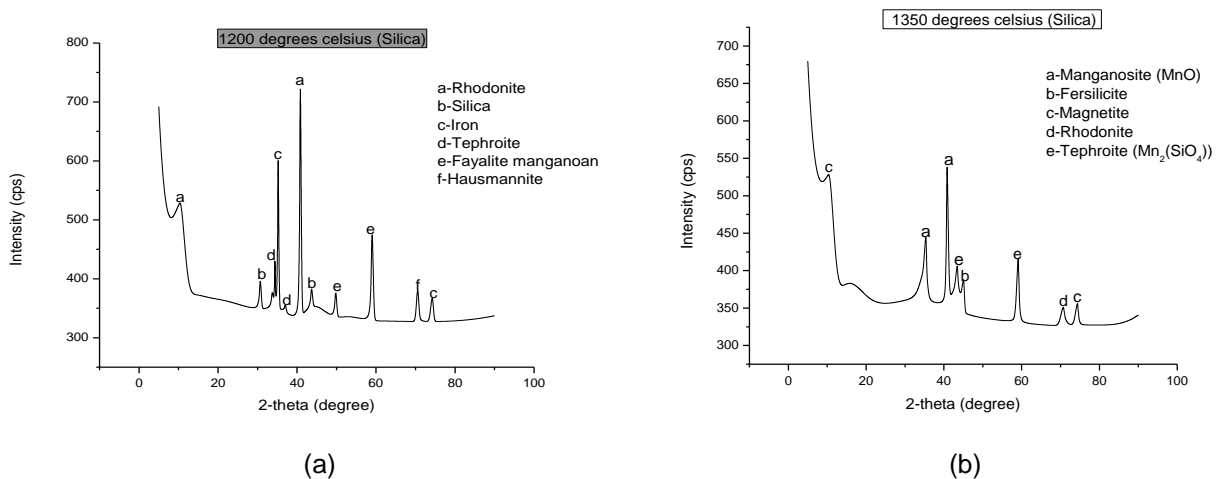


Figure 3 XRD spectrums with silica addition

The addition of silica has favoured the formation of fayalite manganese at lower temperature than when alumina is added since more silica is present. Tephroite is also depicted. This phase also formed when alumina was used as fluxing agent. However, the fraction of tephroite is less than that of rhodonite. The decrease of A/S ratio favours the decomposition of tephroite. Further, the presence of hausmanite in the sample is a confirmation of a barrier caused by the formation of rhodonite since the reduction has not led to more MnO.

It is well known that the addition of an acidic oxide to a basic oxide lowers the melting point. It is here observed that, with the increase of mole fraction of silica, the liquidus temperature is lowered and the formation of MnSiO₃ (rhodonite) is favoured and is predominant than tephroite. Therefore, for basic South African manganese ore (Nchwanging), it is observed that rhodonite formed during prereduction. It was however important to note that the formation of manganese silicates phases hinder the reduction of MnO. It is therefore understood that manganese silicates phases are acting as barriers to the MnO reduction. Also, since the addition of silica promotes the formation of manganese silicates phases mainly rhodonite, it is observed that part of the initial manganese oxide (hausmanite) still remain unreduced. This confirms that rhodonite constitutes a barrier to

the reduction of MnO therefore reduces the activity of MnO in the slag. It can be stated that the addition of silica increased the activity of silica but decreased the activity of MnO in the slag.

The presence of rhodonite was explained by the decomposition of tephroite. At this stage, due to the formation of more liquid slag, the presence of manganosite and the addition of silica, MnSiO₃ slows the reduction of MnO because it covers MnO particles as explained earlier. As a consequence, the reactivity of MnO is therefore reduced [7]. The reduction of silicious Groote Eylandt studied by previous researchers, in the temperature range of 900 to 1400 °C, it was found that the calculated diffusion coefficient of MnO present in the slag around 1400 °C was smaller than the one when basic Mamatwan manganese ore [6].

4. CONCLUSION

Two fluxes namely alumina and silica were added to the Nchwaning ore to investigate their impact on the slag formation. Experiment were conducted at 1200 °C, 1250 °C, 1300 °C and 1350 °C in presence of carbon. It was found with the basicity kept at 1, that Al₂O₃/SiO₂ (A/S) ratio plays a significant role on the reduction rate during the production of HCFMn using basic manganese ores.

The reduction rate was higher with alumina than with silica addition. The higher the A/S ratio the higher the reduction rate. It was found that this was due to the formation of manganese silicate phases which form barriers around the MnO particles by covering their surfaces rendering MnO less reactive while decreasing the diffusion.

Although the basicity was kept at 1 when the two fluxes were added, it was found that the basicity was not the influential factor that dictates the reduction rate, but rather the type of fluxes.

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