

Slag System with Alumina Addition Between 1200°C And 1250°C During High Carbon Ferromanganese Production

MK. Wa Kalenga and DK Nyembwe

Abstract— During smelting processes, the slag formation is a key parameter for an efficient process. During High carbon ferromanganese production, the slag phase formation starts in the upper zone. The ore composition plays an important role in the slag formation which impacts metal recovery. The addition of alumina on the slag phase formation has been investigated. The characterization of materials has been conducted using XRD and SEM-EDS essentially to identify different phases that were present. The investigated temperature ranged from 1200°C to 1250°C. Results have shown that the slag was predominantly tephroite and that alumina addition did not have major influence on phases that formed.

Keywords— Alumina, High carbon ferromanganese, phases, slag.

I. INTRODUCTION

The chemical composition of an ore determines the route and the steps that would be best for better recovery. While the chemical composition plays a vital role, pyrometallurgical processes focus on the formation of the slag and this not only in the melting zone but throughout the furnace. The formation of the slag starts from a certain level of the furnace, therefore a thorough analysis of formation of phases is paramount. In the case of high carbon ferromanganese production, depending on the type of ore acidic or basic, the choice of flux is important. Although the flux allows the slag to melt at an acceptable temperature, this goes together with favoring the formation of preferential phases that would unlock the targeted metal. During carbothermic reduction of high carbon ferromanganese, it was found that the reduction rate is dependent on the formation of silicates at solid state which inhibit the diffusion of MnO for further reduction by creating barriers around MnO particles [1]. The presence of MnO in solid state plays an important role in the reduction rate [1]. Furthermore, at low silica mole fraction up to 0.32, the manganese silicates decompose with an increase in temperature from around 1310°C, and two phases are produced, a liquid phase and a solid phase rich in MnO. At higher SiO₂ mole fraction around 0.5 and above, a liquid phase and a solid phase rich in SiO₂ are produced with temperature increase.

The activity of MnO in a multicomponent system MnO-CaO-SiO₂-MgO-Al₂O₃, with MnO less than 30%, was found to be dependent on the slag compositions. The substitution of SiO₂ or Al₂O₃ by MgO or CaO on one hand and the increase of the CaO/MgO ratio caused the MnO activity coefficient to increase [2,3].

The reduction of silicious Groote Eylandt studies in the temperature range of 900°C to 1400°C, has revealed that the calculated diffusion coefficient of MnO present in the slag around 1400°C was smaller than in basic Mamatwan manganese ore [4].

At temperatures lower than 1000°C, the stability of higher manganese oxides is directly proportional to oxygen pressure [5].

MnO₂ and Mn₂O₃ are unstable above 730°C and 830°C respectively, with respect to Mn₂O₃ and Mn₃O₄ [6]. The same trend was observed on Mamatwan ores [7,8] which has no MnO₂ [9]. Mamatwan ore is basic as is the Gloria ore used in this base case, but its basicity is much higher - around 4.

With acidic Wessel manganese ore, the reduction of iron to metallic iron started at around 1100°C [10]. It has been demonstrated theoretically that it is possible to predict slag formation of a complex thermochemical equilibrium in manganese reduction using FactSage and have also shown, using FactSage, the prediction of equilibrium in the Coke bed zone and MnO activity calculations based on certain assumptions are possible [11,12].

II. METHODOLOGY

A. Material and equipment

Basic south African manganese ores were used in this investigation. Alumina 98.9%-powder-25 μm sourced from the Department of Metallurgy at the University of Johannesburg; was used as flux and coke containing 87% fixed carbon used as reductant. Experiments were conducted using a THM 15 vertical alumina tube furnace equipped. X-Ray diffraction spectroscopic Rigaku Ultima IV for mineralogical analysis, Scanning electron microscopy (SEM-EDS) TESCAN for morphological analysis.

B. Experimental procedure

The manganese ore was mixed with the stoichiometric amount of coke with alumina added to the mix. The mix was milled for 15 minutes to homogenize the sample. The sample was placed in a graphite crucible which was placed in the hot

Manuscript received 10 October 2024.
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zone of the furnace. Carbon monoxide was blown into the furnace to enhance the reduction and favor the formation of phases to allow alumina to react. The sample was kept in the furnace for two hours after the furnace has reached the aimed temperature. From room temperature to 600°C only argon was blown into the furnace to remove any oxygen, then the argon gas was stopped while the CO gas was switched-on till the aimed temperature. After the two hours, the furnace was switched-off under CO until 600 °C when argon gas was switched-on to room temperature. The products were subjected to XRD and SEM-EDS analysis for phases identification.

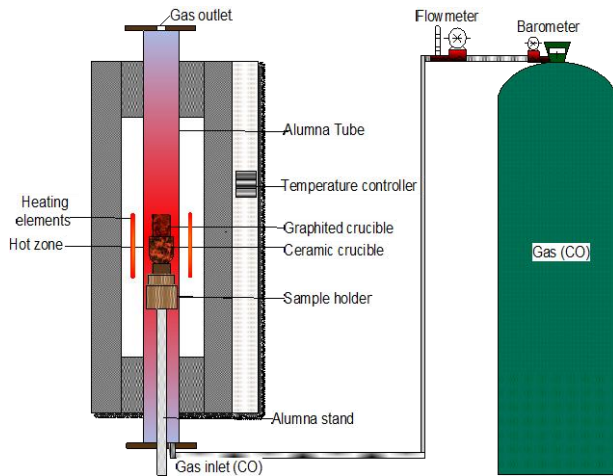


Fig. 1:: Experimental setup

III. RESULTS AND DISCUSSION

A. Influence of alumina at 1200°C on the slag system

Fig. 2 depicts the phases during the carbothermic reduction at 1200°C. The monoxide phase (MnO) exhibits a rapid reduction stage, since no Mn_3O_4 , an intermediate manganese oxide, was detected. This agreed with the predictions in the model. Metallic iron and silicate phases were present. Silicates' presence in the slag of the samples was aligned with the model's predictions. 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 as previously. The presence of MnO (Manganosite) confirmed that Mn_2O_3 reduction had progressed rapidly to MnO.

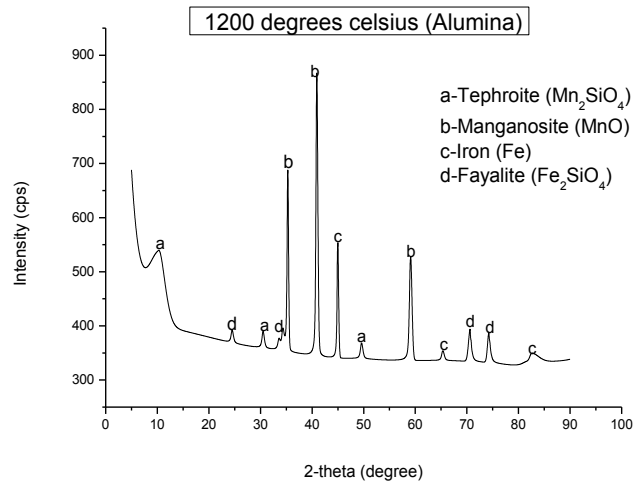


Fig. 2. XRD patterns at 1200°C with alumina addition

This indicates that the rapid reduction stage has taken place. Since alumina in the basic ore used in this investigation head sample is low, Al_2O_3 addition displaces the slag composition from the binary MnO-SiO₂ line inward toward the SiO₂-Al₂O₃ line. At 1200°C, the isotherm in the grey line, in Fig 3; delimiting the investigated area showed the expected phases.

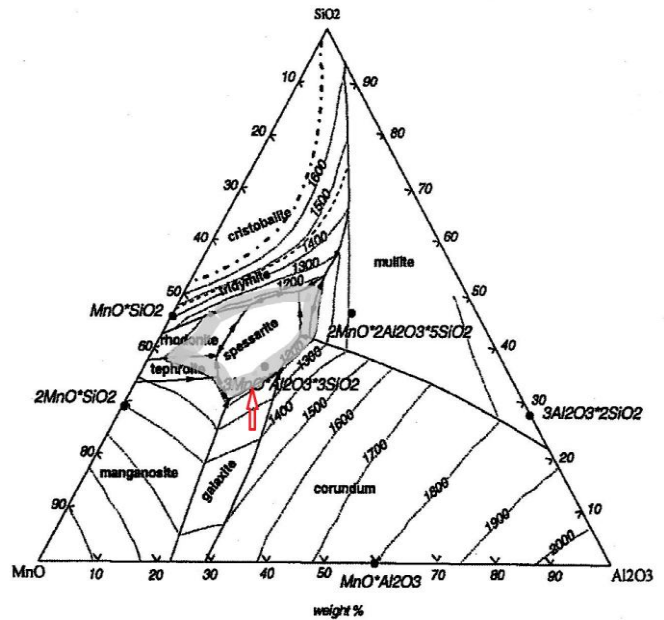
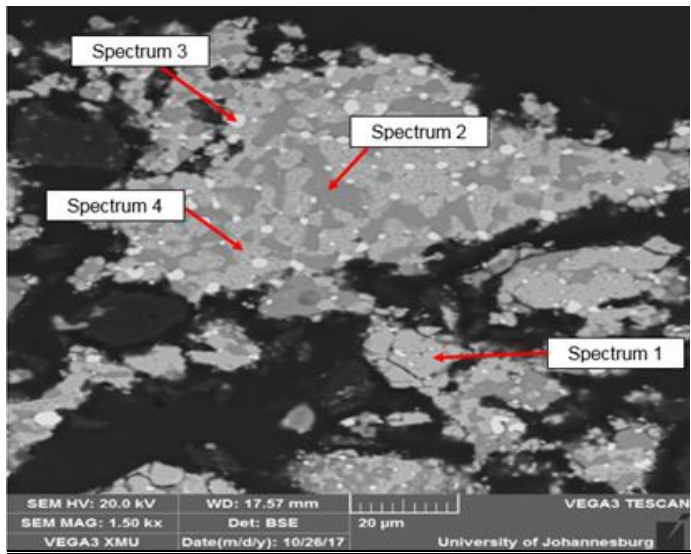


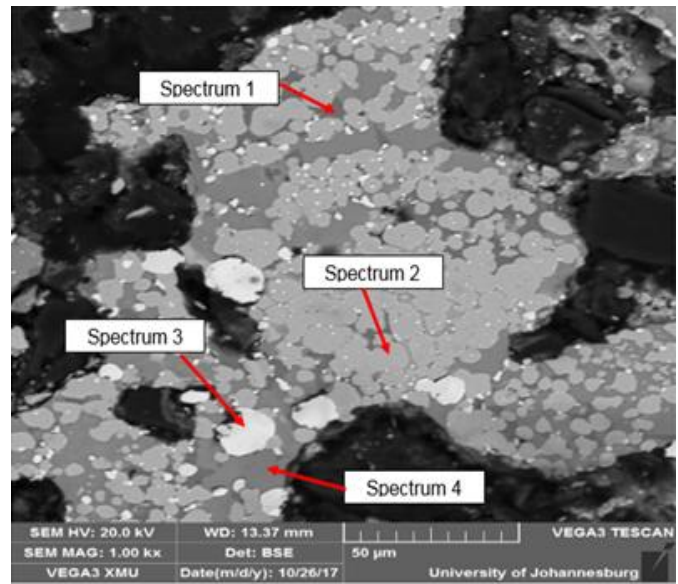
Fig. 3: MnO-SiO₂-Al₂O₃ ternary diagram

From Figure 4 presenting SEM-EDS results, tephroite, rhodonite, spessartite were expected in the working range of temperature. The XRD results are therefore in agreement with the prediction, confirming the presence of tephroite in the sample.



Spec No	F	Mg	Al	Si	Ca	Mn	Fe	O
Spec 1	7.7	0.7	-	-	0.3	59	11	21
Spec 2	4.6	0.8	-	12	25	8.9	6.2	31
Spec 3	-	-	-	-	-	14	86	-
Spec 4	-	0.2	1.7	2.0	3.1	10	58	25

Fig. 4: SEM micrograph of the sample reduced at 1200°C with alumina addition



Spec No	F	Mg	Al	Si	Ca	Mn	Fe	O
Spec 1	-	0.2	15	11	26	5.6	0.3	37
Spec 2	4.0	0.8	-	-	-	73	-	22
Spec 3	-	-	-	-	-	22	79	-
Spec 4	3.4	0.8	-	15	19	27	-	34

Fig. 6: SEM micrograph of the sample reduced at 1250°C with alumina.

B. Influence of alumina at 1250°C on the slag system

Figure 5 presents XRD patterns at 1250°C with alumina addition. Except for fayalite, most of the phases depicted at 1200°C remained. Fayalite decomposed with iron reporting to the metal while dissolution of calcium in silica led to the formation of wollastonite (CaSiO₃).

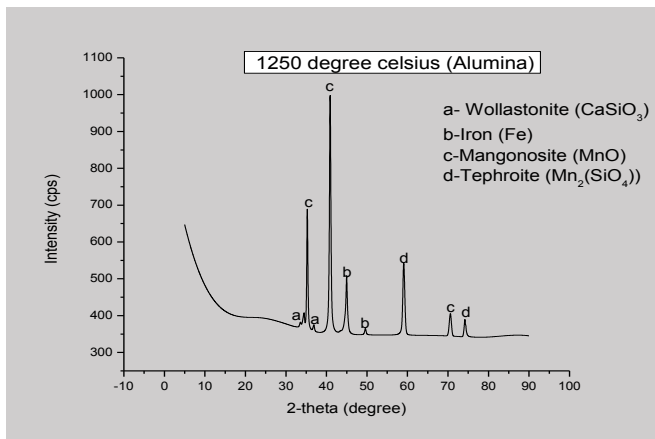


Fig. 5: XRD patterns at 1250°C with alumina addition

It is therefore crucial to note that the formation of silicate phases is predominant.

SEM-EDS results of the products obtained at 1250°C with alumina addition are shown in Figure 6.

SEM-EDS results show an increase in Mn content in the alloy while MnO phases are more disseminated with temperature FeMn alloy and tephroite.

IV. CONCLUSION

The influence of alumina on the temperature from 1200°C to 1250°C on the slag system has shown no major change during high carbon ferromanganese carbothermic reduction. Results have revealed that the main phases were predominantly silicates and monoxide of manganese as well as minor ferromanganese. The phases composition did not show any predominance of phases governed by the presence of alumina. Therefore, the choice of a flux would preferably silica in order to reduce the basicity. However, it is important to take into account the fact excessive silica addition has been found to promote the formation of barriers around MnO matrix.

ACKNOWLEDGMENT

The authors are grateful to all the technicians in the Department, University of Johannesburg for their availability and assistance in the laboratory.

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