IMPACT OF Al_2O_3/SiO_2 ON THE SLAG SYSTEM IN THE COKE BED ZONE DURING HIGH CARBON FERROMANGANESE PRODUCTION USING BASIC MANGANESE ORES

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Abstract

During High Carbon ferromanganese production, the slag formation plays an important role on the overall process. Though the slag formation starts in the prereduction zone, silica may be reduced depending on the reducing conditions. Stronger reducing conditions lead to some silicon reporting to the metal. The influence of $Al2O_3$/SiO_2 ratio on the slag in the reduction zone was investigated. The variation of A/S ratio was obtained by adding silica while alumina was kept unchanged. For better homogenization the ore, flux and coke were mixed and milled to -75 microns for 15 minutes. Bench tests scale were conducted using an alumina tube furnace that was programmed at different temperatures. A graphite crucible placed into a silica crucible; the crucible was placed in the hot zone of the furnace. To create more reducing conditions, carbon monoxide was blown into the furnace at a flow of 0.5L/min. Argon was blown into the furnace from room temperature to 600°C then switched off to allow only carbon to react with the oxide ore. The furnace was kept for two hours at the aimed temperature and switched off until the furnace reached 600°C then argon was blown into the furnace down to room temperature. XRD, XRF, SEM and EPMA were used for characterization. An alumina tube furnace was used for the experiments. The temperatures used were 1400, 1450 and 1475°C. The influence of the A/S ratio on phases that formed and the impact on the slag formation in the reduction zone were assessed.

Keywords: Al_2O_3/SiO_2, HCFeMn, coke bed zone, Slag formation

1.   INTRODUCTION

The chemical composition of the feedstock plays an important role in the production of high carbon ferromanganese (HCFeMn) and the quality of the products are largely dependent on it. Number of research on the configuration of furnaces used during the carbothermic reduction of ferromanganese have been investigated especially when acidic manganese ores were used. Furnaces have been stratified and the number of reactive zones were determined by different groups of researchers [1-4]. Full understanding remains a challenge because the chemical composition of the raw materials may vary considerably, therefore investigations are required to adjust the process. Reactions in the upper zones have an influence on the behaviors recorded in the lower zones including energy consumption. Particle sizes were found to have great influence not only on the mechanism but also the kinetics [5]. Efficient control of carbon and stable operations were found to be well monitored during the process when reactive zones were investigated separately [6]. The types of fluxes used and the way they are added to the mix was found to have an effect on the slag formation and the reduction rate and the dissolution of manganese in the slag therefore increasing the manganese loss in the slag [7-8]. In the prereduction zone 1200 °C, using acidic manganese ores; during carbothermic reduction silicates phases formed [9] while increased basicity decreased the reduction rate [10]. It was also reported that diffusion barriers are formed at the MnO reaction interface with the reduced ore when the slag forms therefore the reduction becomes slow [11]. To connect the theoretical knowledge to what is observed in the products, the stratification of the furnace was found important and the behavior due to the chemical composition of the feed including fluxes, it is paramount to investigate the influence of the fluxes on the formation of slag phases

in different active zones. The current investigation researches the influence of Al_2O_3/SiO_2 ratio on the slag system in the coke bed zone when basic manganese ore are used. The temperature varied from 1400 ^oC to 1500 ^oC.

2.   EXPERIMENTAL

2.1.   Materials

Basic manganese ores were used in this work. Silica and alumina are fluxes used and were sourced in the laboratory of the Department of Metallurgy, unibersity of Johannesburg. Argon and carbon monoxide cylinders provided by Afrox Africa. Metallurgical coke was used as reductant.

2.2.   Equipment and experimental procedures

A THM 15 vertical alumina tube furnace with a heating rate of 7 $^{\circ}$C/min and graphite crucibles were used for the experiments. Analytical techniques used for the characterization of the samples, feed and products; were essentially XRD coupled with Topaz and Rietveld and EPMA. The ore was mixed with the stoechiometric amount of coke, the required amount of flux to adjust the basicity to 1. The mix 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 $^{\circ}$C and the valve was switched-off thereafter until reaching the aimed temperature. 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 $^{\circ}$C till room temperature. This to avoid any reoxidation if any. The products were collected and analysed.

3.   RESULTS AND DISCUSSION

The mineralogical results are presented in **Table 1** below.

Table 1 Mineralogical analysis of the manganese ore [12]

Mineral	(wt%)	Mineral	(wt%)
Braunite 1 $Mn^{2+}Mn^{3+}_6O_8SiO_4$	44	Hematite F_e2O_3	9.6
Braunite 2 $Ca(Mn,Fe)_{143}SiO_{24}$	25	Barite $BaSO_4$	1.0
Bixbyte $Mn^{3+}_2O_3$	7	Calcite $CaCO_3$	9.4
Hausmannite	1.8	Manganite $MnO(OH)$	1.7

Results show that Braunite 1 is the major manganese mineral in the sample followed by Braunite, Bixbyte, while hausmanite and manganite. Hematite is the only iron source.

Tables 2,3 and **4** provide EPMA results of the slag formation, with silica addition as fluxing agent; in the coke bed zone at 1400 °C, 1450 °C and 1475 °C respectively. Results at the three different temperatures show that during the formation of the slag in the coke bed zone are very much similar to those that formed in the prereduction zone. At 1400°C, essentially silicates and monoxides are the main phases. Among the silicates present were dicalcium silicates. The formation of orthosilicates $Ca_2Mg(Si_2O_7)$, $CaFe_2SiO_4$ and Fe_2SiO_4 is due to the interaction Ca^{2+}ions with SiO_2 that is strong. It is therefore concluded that the decrease of basicity does not disarrange SiO_2 network.

At 1450 °C, silicate phases that formed were disseminated throughout in the slags. Spectrum no. 3 was one of the smallest metal particles among the spectra analysed. It transpired from the atomic percentage that the smallest metal particle contained the lowest amount of manganese. This was most probably due to a possible reaction between the oxides with dissolved carbon being dissolved in the iron nuclei. From the observation of

the sample of the slag, it was discovered that metal particles of a bigger size were right at the top of the slag. Although earlier findings have shown that high carbon ferromanganese slag does dissolve some carbon [13], from the analysis of the slag in this research no carbon has been found therefore the hypothesis of the reduction of metal by the assumed dissolved carbon in the slag is not supported by the current findings. Previous findings in the prereduction zone where there was no excess of carbon, no metal formed [12], which differs from the current findings where metal particles were present.

At 1475 °C, From the XRD graphs it can be deduced that the kirschsteinite ($CaFe_2SiO_4$) at 1400 °C and 1450 °C was present as a calcium iron silicate. As the temperature increased to 1475 °C the kirschsteinite changed its phase and composition to monticellite $CaMgSiO_4$. Some unreacted carbon can be observed in the sample at analysis points 9 and 59. With the temperature increase, the Fe in $CaFe_2SiO_4$ is substituted with Mg forming $CaMgSiO_4$. Further temperature increases favoured Mg_2SiO_4. Also, the slag structure was flaky with the increase of temperature.

Table 2 EPMA (400x) analysis of slag at 1400 °C with silica addition

spec	Mg	Si	Ca	Fe	Mn	Al	O
49	2.28	14.23	12.16	0.11	13.72	0.09	57.13
50	0.07	8.62	5.77	0.03	12.28	14.67	57.78
51	0.07	8.71	5.96	0.04	11.71	14.62	57.84
52	1.28	0.08	0.65	0.01	47.78	0.13	50.07
53	1.58	0.05	0.66	0.06	44.59	1.52	51.14

at.% at 1400°C (SiO₂)

Table 3 EPMA (400x) analysis of slag at 1450°C with silica addition

spec	Mg	Si	Ca	Fe	Mn	Al	O
1	1.25	14.18	12.06	0.04	15.16	0.06	57.1
2	1.45	0.03	0.58	0.1	47.69	0.1	50.04
3	0.32	10.85	5.11	0.04	12.9	11.99	58.3
4	0.2	9.57	4.22	0.02	16.02	11.91	57.66
5	1.13	14.2	11.91	0.12	15.46	0.07	57.12
6	1.56	0.03	0.6	0.17	47.51	0.08	50.03

at.% at 1450°C (SiO₂)
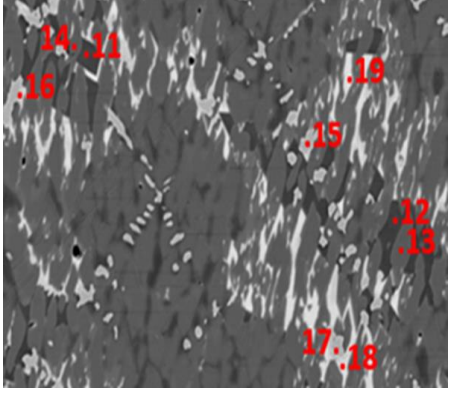
Table 4 EPMA (400x) analysis of slag at 1475 °C with silica addition

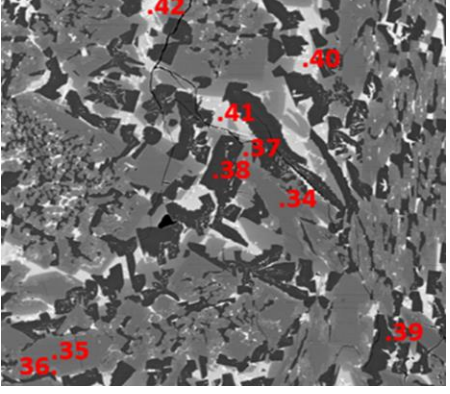| spec	Mg	Si	Ca	Fe	Mn	Al	O
54	1.09	14.8	11.06	0.04	15.85	0.05	57.11
55	1.28	0.03	0.56	0.11	47.92	0.06	50.02
56	0.17	9.57	3.79	0.02	14.72	12.72	57.62
57	0.42	11.06	5.04	0.78	12.13	11.2	57.98

at.% at 1475°C (SiO₂)

Tables 5,6 and **7** show the EPMA results of the slag formation, with addition as fluxing agent; in the coke bed zone at 1450 **°C**, 1470 **°C** and 1500 **°C** respectively.

The general observation is that the influence of alumina on the slag formation in the coke bed zone, there is formation of corundum which also formed in the prereduction zone. However, additional phases were found such as Serendibite, Skiagite alumina and Gehlenite that did not form part of the slag in the prereduction zone.
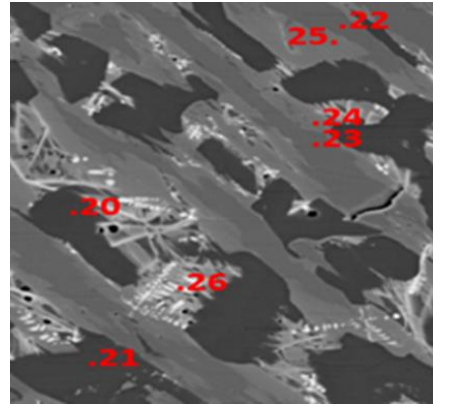
Table 5 EPMA (400x) analysis of slag at 1450 **°C** with alumina addition

at.% at 1450°C (Al_2O_3)							
Spectrum	Mg	Si	Ca	Fe	Mn	Al	O
11	0.19	9.71	15.07	0	1.46	14.94	58.58
12	0.26	9.54	15.25	0.01	1.34	15.04	58.52
13	2.41	13.96	13.59	0	12.74	0.25	57.04
14	2.39	14.05	13.46	0	12.78	0.22	57.08
15	1.08	0.05	0.58	0	48.19	0.06	50.04
17	1.17	0.03	0.54	0	48.16	0.06	50.02
18	0.5	10.77	4.46	0	14.29	11.12	57.94
19	0.45	10.29	4.16	0	15.59	11.02	57.7

Table 6 EPMA (400x) analysis of slag at 1470°C with alumina addition

at.% at 1470°C (Al_2O_3)							
Spectrum	Mg	Si	Ca	Fe	Mn	Al	O
34	3.08	14.11	13.77	0	11.72	0.2	57.11
35	3.21	14.23	13.94	0	11.41	0.08	57.13
36	2.55	14.24	9.66	0	16.36	0.06	57.14
37	2.25	14.28	7.88	0	18.31	0.11	57.17
38	0.86	10.92	15.7	0	1.7	12.15	58.45
39	0.66	10.37	15.64	0	1.48	13.26	58.46
40	0.14	11.79	3.7	0.01	13.11	11.54	58.47
41	0.14	11.05	3.89	0	10.98	13.9	58.65
42	0.03	2.36	1	0	41.98	2.64	51.8

Table 7 EPMA (400x) analysis of slag at 1500°C with alumina addition

at.% at 1500°C (Al_2O_3)							
Spectrum	Mg	Si	Ca	Fe	Mn	Al	O
20	0.96	11.14	15.84	0	1.69	11.82	58.51
21	1.04	11.54	15.79	0	1.74	11.26	58.57
22	3.64	14.21	13.95	0	11.01	0.06	57.12
23	3.56	14.2	13.86	0	11.13	0.11	57.13
24	2.5	14.38	9.35	0.01	16.51	0.05	57.2
25	2.97	14.21	9.51	0	16.14	0.05	57.12
26	0.09	5.13	2.23	0.01	35.64	3.45	53.42

4. CONCLUSION

The formation of the slag in the coke bed zone when silica and alumina were used as fluxes was investigated. It was found that most of the phases that were present in the prereduction zone when silica was added were similar. However, in the coke bed zone, the presence of silicates barriers around MnO were more pronounced than in the prereduction zone. Further, carbon dissolution in the droplets of alloy were found in the coke bed zone. This was explained by the excess of carbon present. Secondly, the addition of alumina presented corundum which was found in the prereduction zone. However, additional phases such as Serendibite, Skiagite alumina and Gehlenite were present. The difference of phases found in the coke bed zone compared to the prereduction zone might be due to liquid state of the slag that allowed more interaction with the metallic phase and the excess of coke that occasioned more reactions.

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