

The characterization and effects of stoichiometric reductants in ferrochromium production from 1200°C to 1550°C

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Abstract

Ferrochrome alloy is mainly produced in submerged-arc furnaces. The reductants used in ferrochrome production include coke, anthracite and char. During ferrochrome production reductants are primarily added for reduction to take place. However it is still questionable as to what happens during times when the carbon charged is not enough, is stoichiometric or excess than the required amount. This work investigated phase formation and phase changes at different reducing temperatures with stoichiometric amount of reductants with stoichiometric amount of reductant. Experiments were conducted at 1200°C, 1300°C and 1550°C. Anthracite and coke were used in this investigation. A comparison of reaction steps, the extent of reactions as well as the mechanisms at the same temperature and soaking time, when coke and anthracite were used are discussed. The characterization was conducted using different analytical techniques to identify the changes in morphologies of the raw materials against the temperature as well as the phases that formed.

Key words: Stoichiometric reductants, characterization, ferrochrome

1 Introduction

South African chromite ores reserves are all located in the Bushveld complex. Submerged-arc furnaces are most commonly used to smelt chromite ores into ferrochrome by using suitable carbonaceous reductants such as coke, anthracite and char. The operation of submerged arc furnaces for ferrochrome production are very complex in both physical and chemical aspects (1). The complexity of feed structure as well as electrical-thermal-chemical interactions in the furnace result in a wide variations of temperature distribution. The control of the furnace is therefore often difficult due to the complex physical and chemical situations in the furnace (2, 3). Due to the complexity and heterogeneity of carbonaceous materials, the choice of appropriate reductant has become difficult and is based on many parameters with the quality of the products being one of them (4). It therefore becomes important to

understand the steps and extend of reactions when a change in chemical composition of the reductant is remarkable. An investigation on coke use for ferromanganese smelting was conducted and more reactive coke was said to enabling Boudouard-controlled reactions effective in higher part of the shaft (5), therefore impacting the phases that form. But in ferrochrome smelting, very little reduction occurs at temperatures below 1200°C, while at 1500°C and above most of chromites are easily reduced. It has been also shown that between 1200°C, and 1500°C there is specific discrimination and that at 1400°C particularly a better discrimination was observed (6). During ferrochrome production, the role of gaseous reduction reactions should not be overlooked. Further, some investigations have shown inconsistent kinetics of reduction by solid carbon and was theoretically explained by the participation of an intermediate gas

phase, carbon monoxide (7). A number of investigations have been conducted on the behaviour of many reductants used in different smelting processes. However, chemical compositions differ from one reductant to another depending on the mine where it was sourced from. The chemical composition therefore leads to differences in the behaviour of reductants. The impact of this would be seen on the reactions extent and phases that form. Studies have shown that anthracite has the highest reactivity since its activation energies are the lowest compared to other reductants (8). Recent simulations investigations have shown that there was no direct and clear correlation between fixed carbon and energy consumption among different South African reductants (9). This led to a conclusion that the choice of carbon material should not solely be based on chemical parameters (10). The current investigation focused on comparing the behaviour of anthracite and coke, with stoichiometric amounts used and the sequences of phases that could form; from 1200°C to 1550°C.

2. Raw materials

Table 2.1: Chemical composition of reductants

Reductants	Anthracite	Coke
Cr ₂ O ₃	0.019	0.078
FeO	1.38	1.38
SiO ₂	11.70	8.45
CaO	0.57	0.56

Reductants	Anthracite	Coke
MgO	0.21	1.28
Al ₂ O ₃	3.98	1.28
P	0.014	0.004
S	0.97	0.002
Fixed-C	71.38	77.41

Table 2.1 above shows the percentage of each oxide as well as the elemental percentages in the reductants. The reductants had fixed carbon was 71% and 77% for anthracite and coke respectively. The phosphorus was low but sulphur content was high in anthracite.

Table 2.2: Chemical composition of the ores

Ore	Small Lumpy	Pellets
Cr ₂ O ₃	34.10	41.0
FeO	20.00	24.0
SiO ₂	16.00	6.63
CaO	2.00	0.5
Al ₂ O ₃	12.59	9.3
P	0.004	0.002
S	0.02	0.02
Cr/Fe ratio	1.5	1.5
Basicity (CaO/SiO₂)	0.13	0.07

Table 2.2 shows the chemical composition of different chrome ores used in this investigation. It can be seen from the XRF results that for both small lumpy and pellets the percentage of Cr₂O₃ was below 50% but above 40% for the pellets and below 40% for the small lumpy. The FeO was below 25% whereas chrome-iron ratio was 1.5. This confirmed the assertion of an investigation

conducted previously, which stated that the South African chromite ores generally contain a maximum of 45% Cr₂O₃ and a chrome to iron ratio of about 1.6:1 (11). The basicity of both lumpy ores and pellets was far below 1. This showed that the chrome raw material used was therefore acidic.

3. Experimental set-up and procedure

The experiments were carried out in a vertical alumina tube furnace. Graphite crucible placed in a silica crucible to prevent any spillages in case the graphite crucible reacts with the feed and got perforated. The raw materials received from ASA metals were small lumpy ores and pellets. The samples were crushed and pulverized to prepare for XRD and microscope analysis as well as the improvement of the reactivity of the feed. The crushed chromite ore was sieved to different sizes. Quartz was also crushed using jaw crusher and cone crusher, then sieved according to different sizes. The reductants used included coke and anthracite and were crushed and grinded and sieved to different sizes. A portion of each reductant was further pulverised for chemical composition analysis. Each material was weighed accordingly and blended then charged into the graphite crucibles. When the temperature aimed was reached, the samples were soaked for 90 minutes. The heating rate of the furnace was 5°C per minute. The samples heated below 1500°C

were immediately quenched in water placed in a bucket next to the tube furnace just after it was removed from the furnace. The aim was to freeze the phases and prevent phase changes which have formed at those respective temperatures. However, samples heated above 1500°C were not quenched since the phases formed at that temperature were stable thermodynamically irrespective of time taken for the cooling. The products were subsequently crushed and mounted in a polished section of epoxy resin for microscope analysis and pulverized for XRD analysis to identify different phases that have formed at different temperatures for the different reductants and compared thereafter. Some pics were very close to each other such that they seemed to be one pic representing many phases. To avoid this, pics that were close to each other were decomposed to fully identify the different phases that formed.

4. Results and discussion

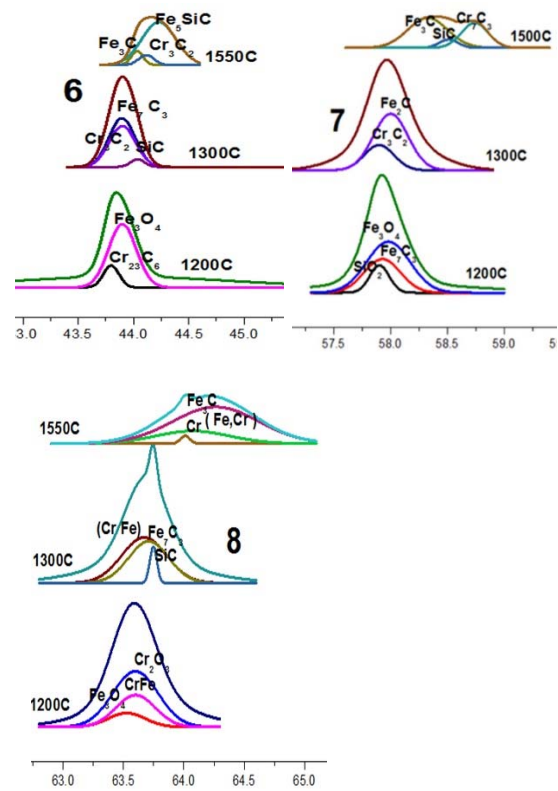
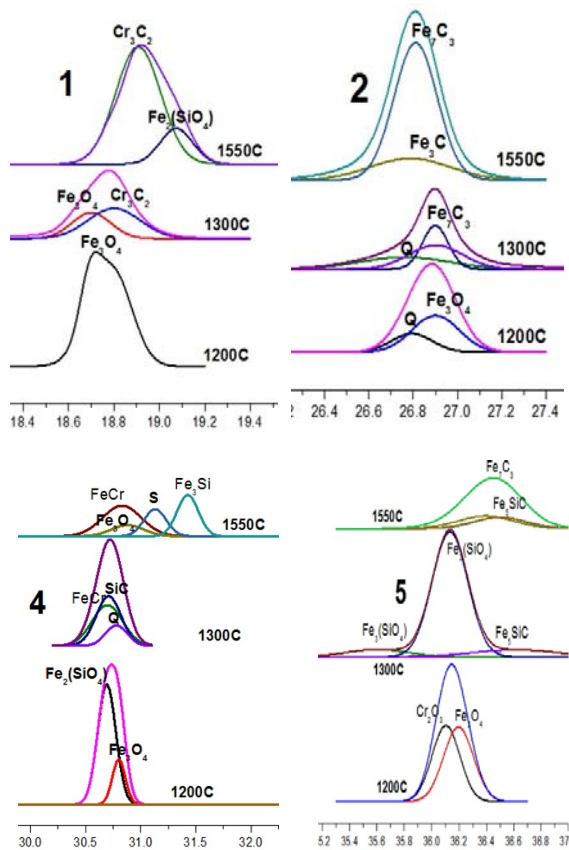
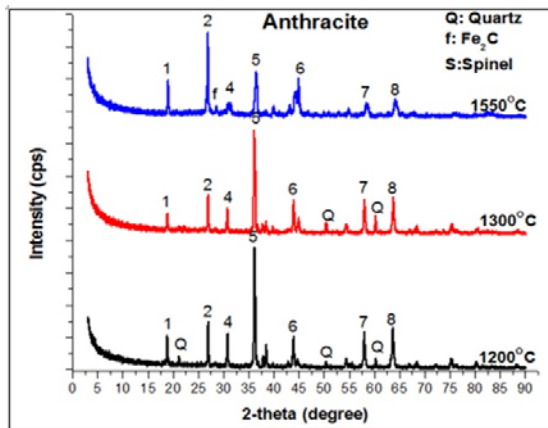
4.1 Properties of reductants

The behaviour of reductants was studied at various temperatures, namely 1200°C, 1300°C and 1550°C. The behaviour studies at these temperatures were recorded by comparing the behaviour of coke and anthracite. X-ray diffraction analysis and optical microscope examination results for

each temperature are shown below for the respective reductant.

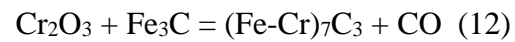
4.1.1 Behaviour of Anthracite

The following graphs show the XRD at different temperatures and from 1 to 8 give information the decomposed picks showing phases that formed when anthracite was used at different temperatures:



From the graphs above the following could be observed: at 1200°C, anthracite showed low levels of reductions. From the qualitative analysis it could be noted that the main phases were Fe_3O_4 , high oxides of chromium, iron carbides that start to form as well as chromium carbides. The presence of these phases simply showed the start of reduction chromite and spinel present in the samples. The formation of iron carbide at this stage showed that some iron was being reduced which then combined with the carbon through diffusion. However, in the presence of Cr_2O_3 and Fe_3O_4 made the carbides metastable. Since there was no liquid present or forming at this stage, the interface present was solid-solid interface hence solid-solid reduction.

diffusion of carbon. These carbides then acted as carbon carriers to ensure further reduction of the chromium oxide into chromium. The most probable reaction that translated the above have been previously reported to have followed the equation:



Phases found to have formed at 1300°C were Fe_3O_4 that remained, Fe_7C_3 , FeC , Fe_2C , Fe_5SiC , FeCr , SiC and Fe_5C_2 in Figures 1 to 8. At the same time it could be seen that fayalite started to form which was an indication of the start of slag forming.

Figure 4.1b: microstructure at 1200°C

On the in Figure 4.1b which represent the microstructure at 1200°C, the dark area A represents the matrix while the grey area B is the unreduced spinel. The picture also depicts secondary spinel C.

Figure 4.2b: microstructure at 1300°C

Figure 4.2b shows the microstructure of chromite reduced by anthracite at 1300°C. The white dots represent the metal phase, light grey area represents the partially reduced chromite and dark grey area represents the gangue phases. At 1300°C, anthracite shows more reduction of chromium oxide into chromium, chromium carbides started forming and more iron carbides appearing. This was explained by the fact that the temperature has increased which implied an increase in the diffusion rate as a consequence. This allowed a faster

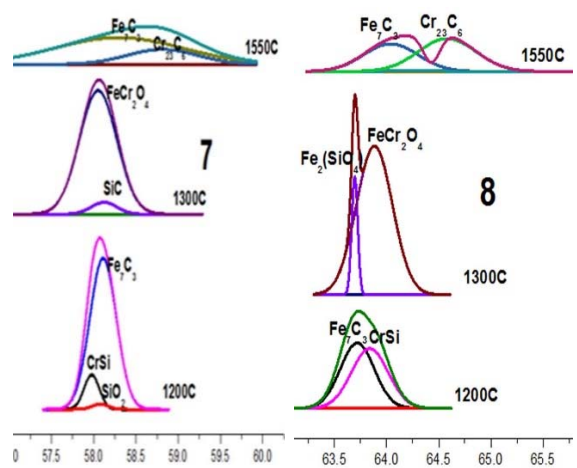
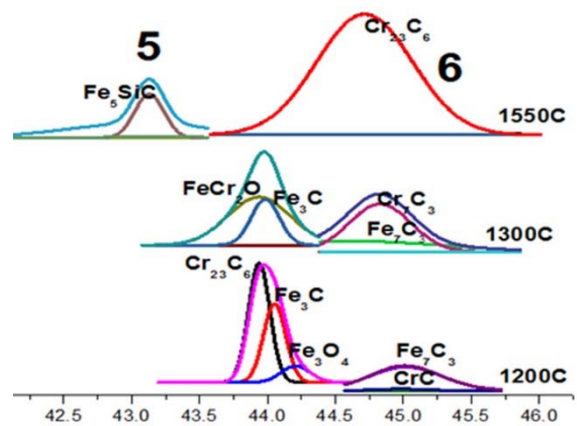
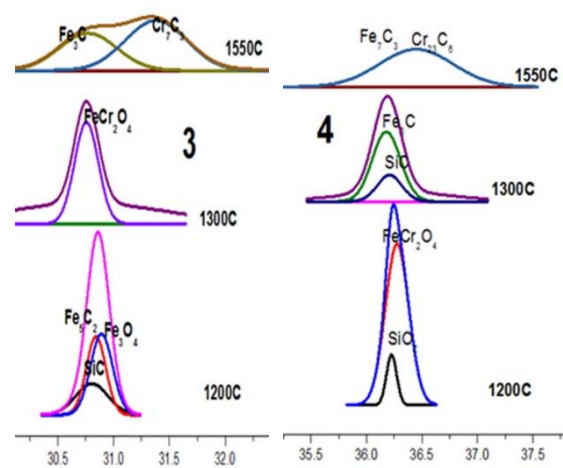
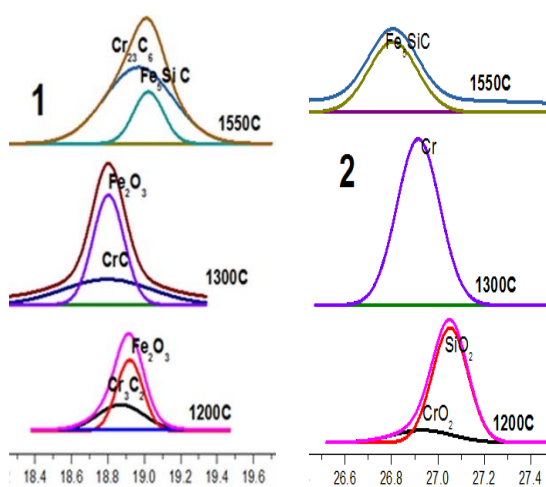
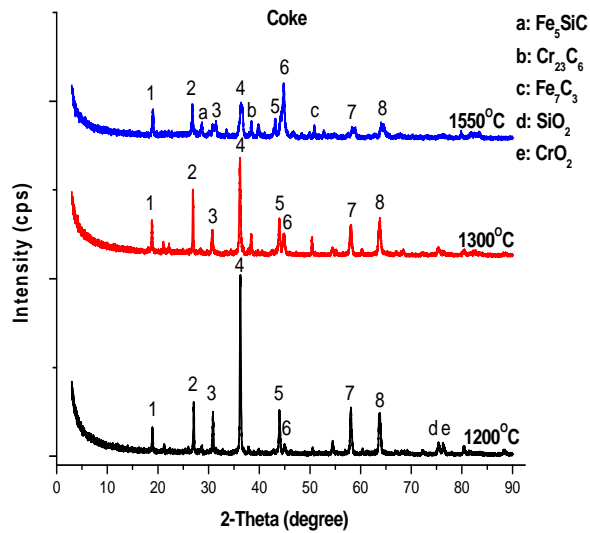
Figure 4.3b: microstructure at 1550°C

Figure 4.3b shows a microstructure of chromite ore reduced by anthracite at 1550°C. The dark area being the slag and the white part being the ferrochromium. From the picture it can be seen that there is some metal in the slag which can be an indication of reduction of oxides into metal. Figures 1 to 8 have clearly shown that at 1550°C the metal FeCr was produced and more carbides, namely Fe_2C , Cr_3C_2 , Fe_7C_3 , Fe_3C , Cr_7C_3 , SiC , FeSiC and Fe_5SiC have formed. Also, it could be seen that the slag formed thus the presence of fayalite as well as of a spinel phase. The presence of chromium

carbides such as Cr_3C_2 and Cr_7C_3 were a good indication of solid state reduction of the ore. Similar results were found in previous research works (13).

4.4.3 Behaviour of coke

The following XRD results showed the behaviour of coke at different temperatures. On all the Figures the bottom, middle and upper lines showed the phases that formed at 1200°C, 1300°C and 1550°C respectively.



From the graphs above the following could be observed:

At 1200°C, coke also showed low level of reductions with the presence spinel phase. However unlike with anthracite, with the use of coke more carbides formed. This was an indication that more reduction place than

when anthracite was used. Fe_7C_3 , Cr_{23}C_6 were common carbides formed at 1200°C when both anthracite and coke were used. However, additionally to the above mentioned common carbides, more carbides namely Fe_5C_2 , Fe_7C_3 , SiC , CrC and Cr_3C_2 formed 1200°C when coke was used. Further, it was observed that SiC , Fe_7C_3 and Cr_3C_2 already formed at 1200°C when coke was used but could only start to appear at 1300°C with the use of anthracite. However, the presence of carbides was a good indication of solid state reduction of the ore when both reductants were used.

However some spinel are partially reduced to form carbides. Figure 2 showed the presence of chromium phases at 1300°C .

Figure 4.4b microstructure at 1300°C

Figure 4.4b above shows the microstructure at 1300°C when coke was used. Partially reduced spinel (PRS) phase, the slag that started to form as well as shiny metal drops (M) were depicted. Although for anthracite and coke metal drops could be depicted at 1300°C , the amount and size of metal drops when coke was used were more than with anthracite use.

Figure 4.4b microstructure at 1550°C

Figure 4.4b shows the phases present at 1550°C when coke was used. It can be seen that coke was more effective than both anthracite at 1550°C .

5. Conclusions

At 1200°C : Anthracite showed lower levels of reductions with dominant phases being spinel, iron carbides and chromium carbides in small amounts. Although the presence of these phases was confirmed, it was observed that there was still some chromite and hematite unreduced. The formation of iron carbide at this stage also showed that some iron was being reduced which then combined with the carbon through diffusion. At 1300°C : Anthracite showed reduction of chromium oxide into chromium. This was attributed to diffusion with then increase of temperature. In other words carbon diffused much more with increasing temperature, thereby forming more chromium and iron carbides, which then acted as carbon carriers leading to further reduction of the chromium oxide into chromium. The results showed spinel phase, silicon carbide and iron carbides phases. Based on the fact that

carbides generally act as carbon carriers it could therefore be believed that with increased temperature, oxides were expected to be reduced by these carbides thus leading to more metal. With the use of coke, it was observed that the amount of chromium increased and partially reduced spinel surrounded by secondary spinel. Also, more chrome metal was detected.

At 1550°C: With the use of anthracite, it was observed some metal was present disseminated in the slag which assumingly was an indication of reduction of oxides into metal, FeCr phases were present. Also iron carbide, chromium carbide and chromium as a metal were present. With the use of coke, it was observed that amongst the phases formed FeCr was present. From the results found in this investigations, it could be seen and concluded that coke was more effective reductant than anthracite at 1823K (1550°C). Further, from the chemical analysis in Table 2.1, the fixed-C was higher in coke than anthracite, this is a major contributing factor in the reductions studied in this investigation.

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