Carbothermal Solid State Reduction of Manganese Ores: 3. Phase Development

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The paper considers phase development in the process of solid state carbothermal reduction of Wessels (South Africa) and Groote Eylandt (Australia) manganese ores in inert gases and hydrogen. Reduction starts with reduction of higher manganese oxides to MnO and iron oxides to metallic iron. When the graphite content in the graphite/ore mixture was in excess relative to the stoichiometric ratio, the final reduction product was (Fe, Mn)7C3 carbide. In the process of reduction of Groote Eylandt ore, silica also was reduced. In the reduction of high silica-ore, manganese oxide was predominantly reduced from tephroite and rhodonite. Silicon in the alloy was present in the form of ferro-manganese-silicon carbide and silicide (Fe, Mn)5Si3.

KEY WORDS: manganese ore; phase composition; Groote Eylandt ore; Wessels ore.

1. Introduction

This is the final paper on solid state carbothermal reduction of Wessels (South Africa) and Groote Eylandt (Australia) manganese ores, of which the composition is presented in Table 1. Two grades of Groote Eylandt ore were examined, which are marked as GE-PF and GE-PS. GE-PS ore contained high silica concentration, 34.4 mass%.

Chemical and phase composition of these ores was discussed in paper1); their reduction in different gas atmospheres was presented in paper.2) Reduction of pure manganese oxide to manganese carbide Mn7C3 in CO atmosphere (P_CO/H2=1 atm) starts at 1 340°C. At this temperature, manganese ore consists of MnO oxide (or MnO–MgO solid solution) and liquid slag, and reduction proceeds through the liquid slag; it includes reduction of MnO dissolved in the slag and dissolution of MnO into the slag. When MnO content decreases below the saturation level, the reduction rate decreases, resulting in high MnO content in the industrial ferromanganese slag. Reduction in the solid state, at temperatures 1 200°C and below, is thermodynamically feasible at decreased CO partial pressure (0.167 atm at 1 200°C). It was demonstrated in work,2) that solid state reduction of manganese ores proceeds with a higher rate in hydrogen than in an inert atmosphere (argon or helium).

The ore reduction behaviour strongly depends on the ore chemistry. Wessels ore was solid at temperatures up to 1 250°C and GE-PF ore up to 1 200°C; GE-PS ore started to melt at about 1 100°C, it was semi-molten at 1 200°C. In the reduction of GE-PS ore at 1 200°C, MnO was predominantly reduced from tephroite and rhodonite. Silica in Groote Eylandt ore was also reduced.

Literature on reduction of manganese ore focuses on industrial processes, in which, as mentioned above, MnO is reduced from liquid slag. This paper discusses development of phases in the process of reduction of manganese ores in the solid state.

2. Experimental

The development of phases in the process of reduction was studied by quenching of reduced samples and analysing phases formed at different reduction stages by XRD, optical and electron microscopy. Experimental set-up and procedure used in reduction experiments were presented elsewhere.2) XRD analysis was done using Siemens D5000 X-Ray diffractometer with a Cu-Kα X-ray source and a nickel monochromator. The scans were done from 20° to 70° at 1°/min and a step size of 0.02°. The voltage used was 30 kV, with a current of 30 mA. The XRD patterns...
were analysed using “Traces” software from Diffraction Technology with JCPDS-PDF2 database. Optical photomicrographs were obtained using a Nikon Epiphot 200 (Nikon Corp., Japan) inverted stage metallurgical microscope with an attached Nikon DXM1200 digital camera. Images were captured using the Nikon ACT-1 software package. Scanning electron microscopy (SEM) was carried out using a high resolution (1.5 nm) Hitachi S-4500 field emission SEM (FESEM) with a tilting stage, Robinson back-scatter detector. FESEM was used to observe the morphologies and section profile of samples obtained at different reaction stages. Energy dispersive X-ray spectroscopy (EDS) was done using an Oxford Instruments Isis energy dispersive X-ray analyser. This was used for qualitative and semi-quantitative chemical analysis at different points and areas within the samples. The reduced samples were also analysed using the Cameca SX-50 electron microprobe. Standard operating procedure involved a 15 kV accelerating voltage, 1–3 μm beam size and a 20 nA beam current. The microprobe has four multi-crystal wavelength-dispersive spectrometer and was operated with a configuration involving two TAP, LIF and PET diffracting crystals.

3. Results and Discussion

It has been shown in work\(^1\) that the phase composition of products of manganese ore reduction depended on the carbon content in the graphite/ore mixture (Table 2 in\(^2\)). When carbon content in the graphite–Wessels ore mixture was 12–16 mass%, manganese oxide was reduced to metallic α-Mn and ferromanganese carbide (Mn, Fe)$_{23}$C$_6$. In the sample reduced with 18 mass% carbon, only carbide (Mn, Fe)$_{23}$C$_6$ was observed. When carbon content increased to 20 mass% and above, (Mn, Fe)$_{23}$C$_6$ was formed.

Reduction of GE-PF ore samples with 12–14.5 mass% carbon was incomplete; major phases in the reduced sample were tephroite (Mn$_2$SiO$_4$) and low carbon iron-manganese carbides (Mn, Fe)$_{23}$C$_6$; unreduced MnO was also detected. Samples reduced with 15–16 mass% carbon contained high carbon manganese carbide (Mn, Fe)$_{23}$C$_6$ and tephroite. With addition of carbon above 20 mass% the final product contained manganese (ferromanganese) silica-carbides Mn$_3$SiC and (Mn, Fe)$_{23}$C$_6$. Oxides were not detected by XRD.

Manganese silicates were not detected in the GE-PS ore samples reduced with graphite content of 14 mass% and above, although complete MnO reduction (from silicate) was approached only when samples contained 24 mass% C. Two silicon-carbide phases were identified in samples produced with 11–20 mass% C, (Mn, Fe)$_{23}$Si$_3$C$_{14}$, and (Mn, Fe)$_8$SiC. In samples with 25–30 mass% C, manganese silicide (Mn, Fe)$_8$SiC was also observed.

Development of phases in reduction of ore with different carbon content will be illustrated in consideration of Wessels ore. Analysis of phases in the reduction of both grades of Groote Eylandt ore will be presented for only for reduction with excess amount of carbon.

3.1. Reduction of Wessels Ore

Major phases in Wessels ore identified by XRD and EPMA analyses in work\(^1\) were bixbyite, braunite, manganite, hausmannite and calcite. Development of phases in the course of reduction of Wessels ore with 14 mass% C and 25 mass% C in hydrogen at 1200°C can be seen from XRD spectra in Figs. 1 and 2 respectively. Stoichiometric content of carbon in the graphite/ore mixture for reduction of iron and manganese oxides to (Fe, Mn)$_7$C$_3$ is 19 mass%. The reduction started with reduction of higher manganese oxides to MnO and iron oxides to metallic iron by reactions (1) and (2). This stage was very fast and was completed before samples reached the reduction temperature.

\[
\text{Mn}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{MnO} + \text{H}_2\text{O} \quad \text{(1)}
\]

\[
\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O} \quad \text{(2)}
\]

After 10-min of reaction, analysis of both samples reduced with 14 mass% and 25 mass% C revealed the presence of two phases, unreduced MnO and ferromanganese carbide (Mn, Fe)$_{23}$C$_6$, which was formed by reaction (3).

\[
x\text{MnO} + y\text{Fe} + 10x/3 \text{C} = 1/7 (\text{Mn}_x\text{Fe}_y)\text{C}_3 + x\text{CO} \quad \text{(3)}
\]

Residual manganese oxide in a sample with carbon content of 14–18 mass% C at later stages reacted with (Mn, Fe)$_{23}$C$_6$ forming (Mn, Fe)$_{23}$C$_6$ by reaction (4) (Fig. 1).

\[
(\text{Mn, Fe})\text{C}_3 + \text{MnO} \rightarrow (\text{Mn, Fe})_2\text{C}_6 + \text{CO} \quad \text{(4)}
\]

In a sample with an excess of carbon (above 19 mass% C), all iron and manganese oxides were reduced to high carbon carbide (Mn, Fe)$_{23}$C$_6$ (Fig. 2). Terayama and Ikeda\(^3\) observed in carbothermal reduction of pure MnO, that when carbon/MnO ratio was below stoichiometric, metallic manganese was formed by reaction of Mn$_7$C$_3$ with MnO. When carbon was in excess, the final product of reduction was Mn$_7$C$_3$.

Phase development in the course of reduction of manganes ore was also studied using EPMA. Samples were produced in experiments at 1200°C in hydrogen with 25 mass% graphite at different reduction stages. Analyses of several hundred points were divided into two groups: the metallic and oxide/slag phases. Development of metallic

| No. (Phase) | O | Al | Si | Mn | Fe |
|------------|---|----|----|----|----|
| 1 (Metal)  | - | -  | -  | 77.5 | 21.4 |
| 2 (Metal)  | - | -  | -  | 72.4 | 25.1 |
| 3 (Metal)  | - | -  | -  | 70.9 | 26.8 |
| 4 (Metal)  | - | -  | -  | 82.9 | 11.6 |
| 5 (Slag)   | 49.4 | 15.4 | 35.1 | -  | -  |
| 6 (Slag)   | 50.6 | 16.1 | 34.6 | -  | -  |
| 7 (Oxide)  | 48.0 | -  | 51.3 | -  | -  |
| 8 (Oxide)  | 45.0 | 1.1 | 51.7 | -  | -  |

Note: carbon in the metal phase is not included.
phase in the progress of reduction of Wessels ore is shown in Fig. 3. In the beginning of reduction (degree of reduction <50%, reaction time 10–15 min) the metal phase was enriched with iron which points out that formation of metal phase started with nucleation of iron as a result of reduction of iron oxide by reaction (2) which can also be seen in optical image (Fig. 4). Carbon content in the metal phase at this stage varied over a broad range giving a variety of carbides including (Mn, Fe)\textsubscript{7}C\textsubscript{3}.

Further reduction led to an increase in manganese content in the metal phase (increasing Mn/Fe ratio), while carbon content varied from 7 at% to 30–35 at%. Such high carbon content could be a reflection of graphite presence in the sample.

A major metal phase in samples with an extent of reduction >80% was high carbon manganese-iron carbide (Mn, Fe)\textsubscript{7}C\textsubscript{3} (Fig. 3 at 30 min) with Mn/Fe molar ratio 4.85.

A major change in chemical composition of the oxide phase during 30-min reduction was the depletion of iron in the oxide/slag phase.

Changes in morphology of Wessels ore in the process of reduction are illustrated in Figs. 4 and 5. Common trends in morphology transformation correspond to the reduction stages. Nucleation and growth of a metallic phase is seen in Fig. 4(b). When degree of reduction was in the range 50–80%, a breakdown of oxide particles into smaller oxide blocks with the size 10–50 μm was observed (Fig. 5(a)) as well as further growth of the metal phase (Fig. 5(b)). In the final reduction stage, reduction of small oxides blocks was accompanied by sintering of the metal phase (Figs. 5(c) and 5(d)). Practically, described processes occurred simultaneously, although with different extent. For example, in a sample with the degree of reduction more than 80% a small fraction of ore grains just passing nucleation stage was observed. Such asynchronous reduction across ore particles was due to their non-uniform morphology and chemistry.

3.2. Reduction of GE-PF Ore

Major phases in the GE-PF ore were pyrolusite, manganese and iron silicates, and silica.\textsuperscript{11} Stages of carbothermal reduction of the GE-PF ore in hydrogen at 1 200°C can...
be identified from XRD patterns of samples in the progress of reduction (Fig. 6). In the first 5 min, when a sample was heated up to 1000°C, pyrolusite was reduced to MnO and iron oxides to metallic iron (reactions (2) and (5)).

\[ \text{MnO}_2 + \text{H}_2 \rightarrow \text{MnO} + \text{H}_2\text{O} \] ......................(5)

After 10 min of reduction, XRD spectra contained peaks of MnO, tephroite and carbide \((\text{Mn,Fe})_7\text{C}_3\). The carbide phase became predominant after 30 min of reaction, although MnO and tephroite were still detectable by the XRD analysis (Fig. 6). MnO and tephroite peaks were not observed on the XRD spectrum of a sample after 40 min of reduction. XRD analysis of this sample detected carbides \((\text{Mn,Fe})_7\text{C}_3\) and \((\text{Mn,Fe})_5\text{SiC}\). Although the oxide phase was not observed in the XRD spectra of reduced samples, it was well identified by the EPMA analysis.

The reduction of solid MnO phase in the GE-PF ore to ferro-manganese carbide was similar to that of Wessels ore and pure manganese oxide MnO: nucleation and growth of nuclei (Figs. 7(a) and 7(b)) with the reduction of smaller oxide blocks (Fig. 7(c)).

In some particles, a slag phase blocked the solid manganese oxide phase, hindering its reduction. This is seen in Fig. 8; slag started to form with the onset of reduction; however, the MnO phase was not surrounded by the slag until it was reduced to a significant degree. The remaining
MnO phase was engulfed by the slag; it was entrapped inside the slag shell which retarded further reduction. Then, MnO was reduced from the slag by reaction (6) at a lower rate. On the XRD pattern the slag phase is identified as tephroite Mn2SiO4 (Fig. 6, 10 min of reduction).

\[
\text{MnO(slag)} + \text{C} \rightarrow (\text{Mn}, \text{Fe})_7\text{C}_3 + \text{CO} \quad \text{.........(6)}
\]

Phases formed in the reduction of the GE-PF ore with involvement of the slag phase are shown in Fig. 9; their composition is given in Table 2. Three phases are observed in Fig. 9: manganese oxide MnO, slag (manganese silicate) and ferromanganese carbide. Metal phase was predominantly formed in contact with the slag phase, what indicates that MnO was reduced from the slag; this process was accompanied by dissolution of MnO phase into the slag. MnO phase became undetectable by XRD after 40 min of reduction (Fig. 6); further MnO was reduced only from the silicate slag.

With depletion of manganese oxide MnO in the slag phase, silicon started to reduce, and reduction proceeded with the formation of manganese-iron-silicon-carbide phase (Fig. 6). The relationship between silicon and carbon contents in the carbide phase is shown in Fig. 10. Iron-manganese silicon carbide was also well identified after 30-min of reduction by SEM/EDS analyses.

EPMA analysis showed that the final phase composition in the metal phase varied from particle to particle and could be either manganese-iron-silicon-carbide or a combination of manganese-iron carbide and manganese-iron silicon-carbide.

Carbothermal reduction of GE-PF ore in an inert atmosphere at 1 200°C was not complete; the degree of 3-h reduction in helium was 80%. Iron-manganese carbide was observed by XRD after 70-min of reduction. Silica was not reduced; iron-manganese-silicon carbide was not detected by XRD analysis or EPMA.

3.3. Reduction of GE-PS Ore

Groote Eylandt GE-PS ore (siliceous fines) contained a high concentration of silica, 34.4 mass%. Major phases in GE-PS ore were pyrolusite, iron silicate, cryptomelane and silica. This ore started to melt at a relatively low temperature of 1 100°C. At this temperature, reduction was incom-
complete; it reached 90% after 180 min reaction in hydrogen; the degree of reduction was much lower in helium (below 50%) and argon (below 30%).

The main stages of carbothermal reduction of GE-PS in hydrogen at 1 100°C can be identified from XRD patterns in Fig. 11. Reduction of GE-PS started with fast reduction of high manganese oxides to MnO and reduction of iron oxides to metallic iron; most of the SiO₂ phase remained intact. Tephroite and traces of ferromanganese carbide were detected after 10 min of reduction. Manganese oxides were reduced to ferromanganese carbide (Mn, Fe)₇C₃ and reacted with silica to form tephroite; MnO was not detected in XRD spectra after 60 min. Further reduction included reduction of manganese oxide from tephroite.

Carbothermal reduction of the GE-PS ore at 1 200°C was affected by slag formation. XRD spectra of samples taken at different reduction stages are shown in Fig. 12. Ferromanganese carbide (Mn, Fe)₇C₃ was detected after the first 10–15 min of reaction. MnO was not observed on the XRD spectrum of a sample after 15 min of reaction. Major phases at this stage were tephroite and silica. SEM and EDS analyses (Figs. 13 and 14, and Tables 3 and 5) identified two types of particles formed at this stage. A major type (Fig. 13, Table 3) contained ferromanganese carbide enriched with iron, tephroite and MnO–SiO₂–Al₂O₃ slag. The second type of particles (Fig. 14, Table 4) in addition to these phases contained MnO, which was virtually encapsulated into the bulk of the slag phase. These particles contained higher MnO and lower iron content in comparison with particles of the first type.

High iron content in the ore particles stimulated nucleation and growth of the metal phase. Further reduction of MnO proceeded from the slag. Typical EPMA analysis results of a sample at this reduction stage are presented in Table 5. Tephroite was converted to rhodonite by the reaction:

\[
2\text{MnO} \cdot \text{SiO}_2 \rightarrow \text{MnO} \cdot \text{SiO}_2 + \text{MnO} \quad \text{(7)}
\]
MnO formed by this reaction was reduced to the carbide phase.

Silicon was also observed in the metallic phase from the beginning of reduction. Carbides \((\text{Mn, Fe})_x\text{Si}_y\text{C}_z\) of different compositions were identified by EPMA after 30 min of reduction. Ferro-manganese-silicon carbide in close contact with \((\text{Mn, Fe})_7\text{C}_3\) carbide is seen in Fig. 15. Carbon and silicon content in the metallic phase after 15 min and 60 min reduction is shown in Figs. 16 and 17. After 30–40 min from the beginning of reduction, carbon in the manganese-iron carbide \((\text{Mn, Fe})_7\text{C}_3\) was gradually replaced by silicon reduced from the slag phase. This process was very slow; when reduction lasted longer than 150 min, ferro-manganese silicide \((\text{Mn, Fe})_5\text{Si}_3\) was formed (Figs. 12 and 17). The relationship between carbon and silicon concentrations followed a trend established for manganese alloys.4)

### 4. Conclusions

In carbothermal reduction of manganese ores in hydrogen, conversion of higher manganese oxides to MnO and reduction of iron oxides to metallic iron was very fast and completed in the process of a sample heating. When the temperature of the sample reached 1 200°C, major phases were oxide MnO and “slag” which was solid in reduction of Wessels ore and partly molten in reduction of Groote Eylandt ores. Iron was dispersed in the particle and acted as nuclei in the process of MnO reduction. Results of study of reduction of Wessels and Groote Eylandt ores can be summarised as follows.

| Table 3 | EDS analysis of selected areas of high iron GE-PS ore particle reduced by carbon in hydrogen at 1 200°C for 15–20 min. |
|---------|---------------------------------------------------------------------------------------------------------------|
| Phase   | O     | Al   | Si      | Mn     | Fe     |
| \((\text{Mn, Fe})_x\text{C}_y\) | 62.0  | -    | 37.9    | 16.8   | 83.2   |
| \SiO_2  | 49.9  | -    | 15.6    | 35.0   | -      |
| \text{Mn}_3\text{SiO}_5 | 55.5  | 4.66 | 23.7    | 12.4   | -      |

| Table 4 | EDS analysis of selected areas of low iron GE-PS ore particle reduced by carbon in hydrogen at 1 200°C for 15–20 min. |
|---------|-------------------------------------------------------------------------------------------------------------------|
| Phase   | O     | Al   | Si     | Mn | Ti |
| \text{MnO} | 42.8 | -    | -      | 57.0 | - |
| \text{Mn}_3\text{SiO}_5 | 49.5 | -    | 16.0   | 35.2 | - |
| \text{MnO-SiO}_2-Al_2O_3 slag | 58.8 | 5.47 | 21.4  | 9.8 | 2.62 |

| Table 5 | Typical EPMA results of a sample with MnO reduction from the molten slag. |
|---------|---------------------------------------------------------------------------|
| Phase   | C          | O     | Si    | Al | Mn | Fe |
| Slag    | -          | 59.7  | 19.4  | 0.3 | 20.5 | - |
| -       | 60.8       | 17.2  | 3.7   | 16.3 | - |
| \((\text{Mn, Fe})_x\text{C}_y\) | 22.2 | -    | -     | -  | 62.7 | 14.9 |
| 22.5    | -          | -     | -     | -  | 60.8 | 16.7 |
(1) Wessels ore contained high concentration of iron oxides, which was reduced to metallic state by hydrogen. MnO was reduced to carbide \((\text{Fe}, \text{Mn})_7\text{C}_3\) by reaction (3). When carbon content in the graphite-ore mixture was 14–17 mass%, further reduction of MnO proceeded via reaction (4) with formation of carbide \((\text{Mn}, \text{Fe})_7\text{C}_3\). This carbide was not observed in the sample reduced with carbon excess; the only detected carbide was \((\text{Mn}, \text{Fe})_7\text{C}_3\). Mn/Fe atomic ratio in the reduced sample was close to that in the original Wessels ore.

(2) GE-PF ore was the richest in manganese; after reduction of higher manganese oxides to MnO and iron oxides to metallic iron, it contained a high fraction of MnO phase, of which the reduction was similar to what was described for Wessels ore. In the process of reduction of this ore, tephroite was formed. Being fluxed with alkanes and other impurities, manganese silicate was partly molten at 1200°C. Reduction of MnO by carbon at 1200°C was close to completion only in hydrogen. The major phase in the reduced GE-PF ore was ferromanganese carbide \((\text{Mn}, \text{Fe})_7\text{C}_3\). In reduction experiments at 1200°C in hydrogen, silica was reduced by carbon of ferromanganese carbide, forming \((\text{Mn}, \text{Fe})_5\text{SiC}\), which had a glassy appearance; however, reduction was incomplete. In the reduction of GE-PF ore in hydrogen at 1100°C and in inert atmosphere at 1100°C and 1200°C, ferromanganese-silicon carbide was not observed.

(3) GE-PS ore contained very high silica concentration, 34.4 mass%. Manganese content in GE-PS was much less than in GE-PF ore; manganese oxide was predominantly reduced from tephroite and rhodonite; the MnO phase in the ore heated to 1200°C in hydrogen was not even detected by XRD. The silica phase present in the ore was still detectable after 150 min of reduction in hydrogen. The final slag contained alumina, silica and manganese oxides. The degree of silica reduction was very high for such low reduction temperature as 1200°C. Silica was reduced to the carbide phase; ferromanganese silicides were also formed. Metallic phase in the reduced sample after 180 min of reduction contained 1.3–1.6 mass% C and 18–21 mass% Si.

(4) The manganese ore chemistry had a strong effect on the ore solid state reduction. First of all, the ore chemistry defines the temperature of liquid phase formation and maximum temperature for the solid state reduction. Increasing CaO/SiO₂ ratio in the ore increased the temperature of formation of the molten phase. Reduction of Wessels and Groote Eyland GE-PF ores with low silica content is feasible in the solid state at temperatures up to 1200°C; while temperature for solid state reduction of high silica Groote Eyland GE-PS ore is limited by 1100°C.

(5) Gas atmosphere had a strong effect on the reduction mechanisms, kinetics and phase development in the course of reduction. Carbothermal reduction of manganese ore had higher rate and degree in hydrogen than that in inert gas atmosphere.

Reduction or pre-reduction of manganese ore in the solid state has a potential to decrease coke and electrical energy consumption in the processing of manganese ore.

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REFERENCES

1) R. Kononov, O. Ostrovski and S. Ganguly: ISIJ Int., 49 (2009), 1099.
2) R. Kononov, O. Ostrovski and S. Ganguly: ISIJ Int., 49 (2009), 1107.
3) K. Tereyama and M. Ikeda: Trans. Jpn. Inst. Met., 26 (1985), No. 2, 108.
4) N. Anaclito, O. Ostrovski and S. Ganguly: Steel Res. Int., 77 (2006), No. 4, 227.