Reduction Behavior of Manganese Ore Using Methane Gas

Amit Bhalla\textsuperscript{1} and R Hurman Eric\textsuperscript{2}

Branch of Metallurgy and Materials Engineering
University of the Witwatersrand, Johannesburg
Private Bag X3, Wits 2050, South Africa
E-mail\textsuperscript{1}: amitbhalla@gmail.com, E-mail\textsuperscript{2}: rauf.eric@wits.ac.za

ABSTRACT

Reduction behaviour of South African Mamatwan manganese ore using methane-argon gas mixture was investigated experimentally in the temperature range of 1000°C to 1200°C. The effect of changing gas mixture composition, time and temperature was studied using a vertical tube furnace. After each test, three representative samples were prepared; one was analyzed by X-ray diffraction to determine the progress of phase changes, chemical analysis were performed on the second sample to obtain metallization results as a function of each reducing condition for each time interval over the total reduction period of two hours. The third sample was mounted, polished and submitted for SEM-EDAX in order to examine the morphology of the ore and its changes in the course of reduction. It was observed that CH\textsubscript{4} was an effective reductant as it cracked, supplying the reaction site with hydrogen gas and very fine solid carbon. The excess carbon from cracking of methane ensures regeneration of reductants CO and H\textsubscript{2} from reaction product gases of CO\textsubscript{2} and H\textsubscript{2}O ensuring low partial pressure of oxygen at the reaction site. Hydrogen gas may also be involved in the reduction of iron oxide components of the ore. Moreover, depending upon temperature and CH\textsubscript{4}/H\textsubscript{2} ratio in the gas phase the activity of carbon in the system reaches values much higher than unity, shifting the reduction reaction by carbon to lower temperatures. X-rays analysis revealed that manganese ore was reduced primarily to carbide Mn\textsubscript{2}C\textsubscript{3} at lower temperature range of the experiments, but at 1200°C the dominant reaction product was Mn\textsubscript{2}C\textsubscript{2}. At higher temperatures extent of reduction was higher reaching over 75% metallization at 1200°C.

Initial results indicate the possibility of rate being controlled by bulk gas mass transfer to the reaction site for initial stage which was then followed by ionic diffusion rate control. Further experimental work is to be conducted using hydrogen-methane gas mixtures with fixed CH\textsubscript{4}/H\textsubscript{2} ratios in order to study the reduction process where carbon activity is fixed (at much higher values than one).

1. INTRODUCTION

Manganese is probably the most versatile additive in the steel industry and has the added advantage of low cost and easy availability. Manganese can be added in the form of its ore during iron making or as ferromanganese and silicon manganese in the steel making stage. Various types and grades of ferromanganese and silicon manganese, mostly containing from 70 to 90 percent manganese, are produced in large submerged arc furnaces by carbothermic reduction [1-5]. Operation of the SiMn process is often more difficult than the FeMn process because higher process temperature is needed. A process temperature of 1600 to 1650 °C is necessary to obtain metal with sufficiently high content of Si and discard slag with low MnO. The FeMn slag has a relatively low melting temperature (about 1250 °C). Accordingly, when the Mn ore starts melting at around 1350 °C, it will contain a mixture of solid and liquid phase, where the manganese containing solid phase is MnO. Further heating to 1550 °C or more is necessary before the melting ore will mix with the slag and flow freely and for further reduction. The specific power consumption for production of standard SiMn from a mixture of Mn-ore, high-carbon FeMn smelting slag and Si rich metallic remelts can typically be 3500-4500 kWh/ton of metal, depending on the amount of metallic material added to the feed. Each additional 100 kg of slag produced will consume an additional 50 kWh of electric energy [6-10].

This study is investigating solid state reduction of manganese ore by using methane which is likely to contribute to the lowering of energy use and carbon footprint [11-15]. Most of the reduction to metallic state for both iron and manganese units is expected to take place at solid state reduction temperatures mentioned above which would in principle require only a final melting stage to separate the valuable metallic ferroalloy phase from the slag. Thus, it was essential to conduct kinetic studies on manganese ores to reveal the mechanism of hydrocarbon reduction and establish the rate which determines steps leading to process parameters [16-18].

2. EXPERIMENTAL

The South African Mamatwan ore was used for this study. The composition of the ore is presented in Table 1. The manganese particle size, class of -150 μm + 106 μm was chosen for all the reduction tests.
The Fourteenth International Ferroalloys Congress

May 31-June 4, 2015

Kiev, Ukraine

Energy efficiency and environmental friendliness are the future of the global Ferroalloy industry

FUNDAMENTALS, THEORY

Table 1. Chemical Composition of Mamatwan manganese ore.

<table>
<thead>
<tr>
<th>Component</th>
<th>(Mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>37.69</td>
</tr>
<tr>
<td>Fe</td>
<td>4.71</td>
</tr>
<tr>
<td>SiO₂</td>
<td>4.51</td>
</tr>
<tr>
<td>CaO</td>
<td>16.51</td>
</tr>
<tr>
<td>MgO</td>
<td>3.29</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.231</td>
</tr>
<tr>
<td>P</td>
<td>0.0174</td>
</tr>
</tbody>
</table>

The reduction experiments were carried out in a molybdenum wound furnace surrounding a thermo gravimetric (TGA) system from bottom. Details of the experimental setup and procedure are available elsewhere [19]. However, due to the chemical decomposition (cracking) of CH₄ gas at about 550°C much lower than the temperatures employed in this work (1000°C – 1200°C) the TGA could not be used to monitor the reduction reactions. Thus, the progress of the reaction was followed by analytically determining the metallization levels (percentages) of the partially reduced samples at predetermined intervals simply by quenching and removing the samples from furnace. The rest of the experimental procedure was same to those of the previous work conducted in our laboratories [19]. Technical grade argon was used to purge the work tube and acted as a carrier gas for methane. The relative concentration of methane in the argon was changed for different tests. The total gas flow rate was maintained at 880ml/min. Only the manganese and iron oxides were regarded as reducible components of the ore. After each test, three representative samples of the reaction products were split off. One was analyzed by XRD to determine the phase changes. Chemical analyses were performed on the second sample to determine the individual manganese and iron metallization. The third sample was mounted, polished for SEM-EDAX, in order to determine the concentrations (and profile as necessary) of manganese and iron in the individual particles. The experimental variables were time, temperature and concentration of methane in argon.

3. RESULTS AND DISCUSSION

The degree of metallization was calculated using the following equation:

\[
\text{Met}_\text{Mn} (%) = \left( \frac{\text{Mn}^0/\text{Mn}_{\text{Total}}}{} \right) \times 100
\]

\[
\text{Met}_\text{Fe} (%) = \left( \frac{\text{Fe}^0/\text{Fe}_{\text{Total}}}{} \right) \times 100
\]

\[
\text{Met}_{\text{Total}} (%) = \left( \frac{\text{Mn}^0 + \text{Fe}^0}{\text{Mn}_{\text{Total}} + \text{Fe}_{\text{Total}}} \right) \times 100
\]

Where Mn\text{Total} and Fe\text{Total} represent total Mn and Fe in the product expressed as a percent of the total product mass, Mn\text{0} and Fe\text{0} represent metalized Mn and Fe in the product expressed as percent of the total product mass, and Met\text{Mn}, Met\text{Fe}, Met\text{Total} represent manganese, iron and total percent metallization respectively.

Figure 1: Progress of metallization versus time for tests using 10% CH₄ in Ar at T=1100°C.
Energy efficiency and environmental friendliness are the future of the global Ferroalloy industry.

Typical plots shown in Figure 1, Figure 2 and Figure 3 illustrate the progress of metallization as a function of time using 10% CH4 in Ar at 1100ºC, 30% CH4 in Ar at 1100ºC and 1200ºC. Utilizing such plots, xrd analysis, the results of SEM-EDAX and visual observation the following discussion can be provided on the reduction of manganese using a hydrocarbon gas. In 30% CH4 in Ar at 1100ºC showed that Fe metallization decreased with time after first 30 minutes. This decrease seen on the plots may be due the chemical analysis errors. 1200ºC tests using the same gas composition did not reveal such decrease. Further investigation on this issue is in progress.

Total metallization values achieved after two hours ranged from 21% to 72%. The associated Mn/Fe metallization ratios of 0.19 to 0.69 were much higher than those achieved with ordinary solid state carbothermic reduction. The effect of CH4 concentration and temperature did not have a simple direct relationship with the rate and extent of metallization. The most common occurrence was rapid levelling of reduction rate after first 20 or 30 minutes for all CH4 concentration and temperatures revealing that the process will take 20 to 30 minutes to complete the reactions which is much quicker than ordinary carbothermic reduction. It was found that higher reduction kinetics would be achieved when using hydrocarbon gas in comparison to classical carbothermic reduction with excess carbon (Burucu ([20]) at a given temperature. At 1100ºC reduction achieved by carbothermic reduction with excess carbon was around 35% as reported by Burucu [20], whereas from present work it was noted that metallization reached 70% and above at same temperature of 1100ºC.

The XRD analysis revealed that manganese ore was reduced primarily to carbide Mn3C3 at lower temperature range of the experiments, but at 1200ºC the dominant reaction product was Mn6C2.
- The oxide feed material analyzed was detected in the form of: CaMn2O4
- The following phases appeared under most conditions: Mn3C3, Fe7C3 and CaMn2O4.
Specifically, with the progress of metallization, the concentration of the original oxide phase decreased with reduction time and a new oxide phase - Ca₂FeMnO₅ - occurred.
- The Fe₇C₃ appeared as the predominant iron carbide phase early in the reduction test but with progress of metallization, this phase disappeared and was replaced by increasing amounts of Fe₃C.
- Generally, the higher the concentration of methane in the reducing gas, the sooner the Fe₃C appeared potentially due to the higher amount of carbon availability from the decomposition of more CH₄.
- Manganese ore was reduced primarily to carbide Mn₇C₃ at lower temperature range of the experiments, but at 1200°C the dominant reaction product was Mn₃C₂.

The extent of reduction required for each phase to appear was dependent on the reaction time and hence on the percent metallization the sample had undergone, and on the reducing gas composition, temperature and hence the amount of carbon deposited.

The particle morphologies were studied mainly by means of photomicrographs of the back-scatter images under SEM as well as results of the energy dispersive analysis of X-rays (EDAX) across particles under different reducing conditions. Figures 4, 5 and 6 compare the resulting particle morphologies using 10% CH₄ in Ar, 20% CH₄ in Ar, 30% CH₄ in Ar at temperatures 1100°C and 1200°C at times of 20, 30, 60, 90, 120 minutes for 1100°C and 20, 30, 60 minutes for 1200°C. The findings are summarized below:

Changing CH₄ concentration had the effect of changing the kinetic rate and extent of reduction/metallization, and that the CH₄ did not take part directly in the reduction, mainly because it was not stable at these temperatures, cracking around 550°C.

<table>
<thead>
<tr>
<th>Time</th>
<th>10 % CH₄ in Ar</th>
<th>T=1100°C</th>
<th>T=1200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td></td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>30min</td>
<td></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Figure 4: Comparison of particle morphologies using 10% CH$_4$ in Ar at temperatures 1100°C and 1200°C at periods of 20, 30, 60, 90, 120 minutes for 1100°C and 20, 30, 60 minutes for 1200°C.

Comparison of micrographs in Figure 4 together with metallization data reveal the following at 1100°C: product morphologies of particles reacted under 10% CH$_4$ in Ar showed that the extent of metallization was around 20-30% for periods below 60 minutes but increased to above 50% for 90 and 120 minutes and at higher temperature of 1200°C the extent of metallization was higher as seen in Figure 4 at 1200°C for the same gas mixture of 10 % CH$_4$ in Ar.
Energy efficiency and environmental friendliness are the future of the global Ferroalloy industry.

<table>
<thead>
<tr>
<th>Time</th>
<th>20 % CH₄ in Ar</th>
<th>T=1100°C</th>
<th>T=1200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>30 min</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>60 min</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>90 min</td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Figure 5: Comparison of particle morphologies using 20 % CH$_4$ in Ar at temperatures 1100ºC and 1200ºC at periods of 20, 30, 60, 90, 120 minutes for 1100ºC and 20, 30, 60 minutes for 1200ºC.

Comparison of micrographs in Figure 5 together with metallization data reveal the following at 1100ºC: particles reacted under 20% of CH$_4$ in Ar showed that the extent of metallization was around 40-50% for periods below 60 minutes but increased to above 50% for 90 and 120 minutes and at 1200ºC the extent of metallization was higher.

<table>
<thead>
<tr>
<th>Time</th>
<th>30 % CH$_4$ in Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T=1100ºC</td>
</tr>
<tr>
<td>20 min</td>
<td>T=1200ºC</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Comparison of micrographs in Figures 6 together with metallization data reveal the following at 1100°C: product morphologies of particles reacted under 30% CH$_4$ in Ar showed extent of metallization was around 50-60% for periods below 60 minutes but increased to above 70% for 90 and 120 minute and at 1200°C the extent of metallization was higher over 75% for the same gas mixture of 30% CH$_4$ in Ar.

Figures 4, 5 and 6 also revealed that the reduction occurred mostly on the particle surface and metallization due to the formation and/or existence of cracks or pores were very limited. It can also be deduced from the micrographs that at higher temperatures the extent of metallization was higher reaching over 75% at 1200°C.

4. CONCLUSIONS

This study explored the use of different concentrations of CH$_4$ gas in Ar as the reducing gas medium for better understanding of the reduction behaviour of manganese ore at different temperatures. Generally CH$_4$ was an effective reductant because it supplied both C and H$_2$ to the reduction site. The reduction sites were limited to the particle surface and there were no significant crack and pore formation. Very fine carbon was formed with thermodynamic activity well above 1.0 due to cracking of CH$_4$, that ensured the rapid reaction and regeneration of the reductants CO and H$_2$ from CO$_2$ and H$_2$O was formed as a result of reduction reactions ensuring the maintenance of a high reduction potential even
at lower temperature compared to ordinary carbothermic reduction where maximum carbon activity is 1.0. Manganese ore was reduced primarily to carbide $\text{Mn}_7\text{C}_3$ at lower temperature range of the experiments, but at 1200°C the dominant reaction product was $\text{Mn}_3\text{C}_2$. The higher the concentration of the methane in the gasphase, the higher the resulting reaction rate and extent. It can be also deduced that at higher temperatures the extent of metallization was higher reaching over 75% at 1200°C.

5. ACKNOWLEDGEMENT

Authors wish to thank Bhp-Billiton for partially supporting this research work.

6. REFERENCES