High Temperature Behaviour of Iron Carbide

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Key words: Iron Carbide, microscopic characterisation, thermogravimetric analysis

INTRODUCTION

Iron carbide is a new alternative iron source currently that has been produced by Nucor via reaction of fine ore with CH/H2 gas in a fluidized bed reactor. It has the potentially significant advantage over other commercially available iron-carbon sources of being easily transportable, as a fine granular material. Fine granular sources of carbon injected into a steel bath should provide excellent removal of nitrogen because of the large surface area available for CO bubble formation, the CO bubbles acting as an absorbent for dissolved nitrogen in the steel. Trials by Nucor in a number of electric arc furnaces have reported significant removal of nitrogen, from 80 ppm to 30 ppm, without adversely affecting metal quality and with reduced overall energy usage.1,2

In order to gain a better understanding of the basic mechanisms associated with the addition of iron carbide into the melt bath, two commercial iron carbide powders, a sample from the Nucor (obtained in 1997) and another from the Wundowie pilot plant, were characterized using optical microscopy, SEM, XRD and particle size analysis. In addition, thermogravimetric analysis and differential thermal analysis (DTA) methods were employed to investigate the reactions occurring within the iron during heating.

EXPERIMENTS

Chemical Analysis

Chemical analysis for the iron carbide samples was carried out at BHP's Newcastle Laboratory. Total iron was determined by dissolving the sample in hydrochloric acid for reduction by stannous chloride, the excess stannous chloride being oxidized using mercuric chloride. The ferrous iron was then titrated with standard potassium dichromate solution. For the determination of metallic iron, the sample was reacted with bromine-methanol solution to dissolve the metallic iron, leaving oxides undissolved. Following filtration, the filtrate was fumed with sulfuric acid, extracted with water and hydrochloric acid and metallic iron determined by titration with potassium dichromate solution. Ferrous iron was measured by extracting ferrous iron from the sample with hydrochloric acid under an atmosphere of nitrogen into solution, which was then titrated with potassium dichromate.
A Lahnani 8440 Inductively Coupled Plasma (ICP) Spectrometer was employed in determining the minor elements in the material. The sample was dissolved in aqua regia and hydrofluoric acid. Boric acid was added to complex excess hydrofluoric acid. A LECO CS-125 carbon and sulfur determinator, Model 788-400, was used in determining the carbon and sulfur contents in the material. The sample was combusted in an induction furnace and the gas evolved passed through an infrared detector cell to measure the carbon and sulfur content. The repeatability tolerances for blank determinations are ±0.0008% for carbon and ±0.0015% for sulfur. One sample was subject to Mössbauer spectroscopy to determine the iron carbide phase in the sample. This technique has the ability to detect the slight variation in the energy of interaction between the nucleus and extra-nuclear electrons.

**Optical Microscope**

For observation in the optical microscope, powder samples were mounted in bakelite, ground on fine grades of silicon carbide paper, and polished to 1\(\mu\)m. The microstructures were examined with a Nikon reflected light microscope. In order to distinguish different phases in the samples, color etching was applied by etching the polished sample in a thioglycolic acid reagent which attacks cementite but not magnetite, hematite and ferrite. Under the optical microscope, the cementite was colored to brown, but the magnetite remains grey. Different phases in the particles were also distinguished and verified by comparing the obtained Vickers hardness numbers with the standard ones, some of which were listed in Table I.

**Particle Size Distribution**

Screening was used to determine the relative amounts of various particle size in the iron carbide samples, especially for powders with particles larger than 1 mm. Prepared and weighted powders were put through a series of different size sieves, weighing portions of particles in each size range. Original Nucor iron carbide was characterized by this method.

The Wundowie iron carbide powder, which was much finer, and samples to be used for the TG-DTA analysis which were obtained by gently crushing available particles, and further grinding

<table>
<thead>
<tr>
<th>Phase</th>
<th>Load, g</th>
<th>Hardness number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wustite (FeO)</td>
<td>-</td>
<td>250-350</td>
</tr>
<tr>
<td>Magnetite (Fe3O4)</td>
<td>-</td>
<td>450-550</td>
</tr>
<tr>
<td>Fe (FeO)</td>
<td>50</td>
<td>1100</td>
</tr>
<tr>
<td>Cementite (Fe3C)</td>
<td>100</td>
<td>170-220</td>
</tr>
<tr>
<td></td>
<td></td>
<td>595-825</td>
</tr>
</tbody>
</table>

A Leco Microhardness Testing Machine M-400-Ht was employed in measuring the microhardness of the phases.

**Scanning Electron Microscopy (SEM)**

Powder samples were mounted on half inch diameter aluminium stubs and fixed in position using a double-sided graphitized adhesive tape. Samples were then subjected to a 10-second burst in a DYNAVAC magnetron sputter coater (model SC100M) to deposit a thin film of conducting gold on the specimen surface. For phase determination, the particles were mounted in carbon or aluminium bakelit, and following the above polishing step to 1\(\mu\)m. Specimens were then inserted into a Cambridge Leica 440 SEM analyzer, examined to yield maximum contrast, and photographed to keep a permanent record of particular findings. An Energy Dispersive X-ray Spectroscopy (EDX) detector Link ISIS300 system attached to the SEM allowed determination of the chemical composition of the various phases present.
using an agate mortar and pestle, the particle size distributions were measured by a Malvern Mastersizer (Made by Malvern Instruments Ltd., UK) which operates over particle sizes ranging from 0.1 to 1000 \( \mu \text{m} \), based on a light diffraction and scattering principles. The particles must be completely dispersed in a liquid to ensure that one is not measuring the size distribution of particle agglomerates. For iron carbide powders, acetone was found to be effective in improving the dispersability of the particles and reduce inter-particle attractions. The software Mastersizer S Ver. 2.11 was used to control the analyzing process and calculate the relevant parameters such as mean diameters and specific surface area. The statistics of the distribution were calculated from the data collected using the derived diameters \( D[m, n] \) were used on an internationally agreed method of defining the mean and other moments of particle size, according to British Standard BS2955:1993.

**X-ray Diffraction Analysis**

A computerized Philips diffractometer model 1020 (designed for flat powder specimens at room temperature) was used for phase content determination. It comprises a quartz monochrometer to provide CuK\( \alpha \) radiation with wavelength \( \lambda \) of 1.540562 \( \AA \). The diffractogram data were stored and processed by a PC running the program Traces V3.0. The samples were ground into finer powder and then run at a 0.02° step and a speed of 0.5° per minute with a 0.2° slit on the focusing circle. The phase content of the samples was determined by comparing prominent and sharp reflection lines against known values from known substances recorded in the CD-ROM version PDF database (Copyright of JCPDS-ICDD, 1995).

**Thermal Analysis**

A SETARAM TGDTA92 unit, which allows simultaneous TGA and DTA, was used for the thermogravimetric studies. The balance of the unit has a detection limit of 1 \( \mu \text{g} \). The system was fully controlled by an IBM PC through a CS92 controller. The TGA and DTA studies were carried out simultaneously under Ar atmosphere. About 100 mg sample was kept in a alumina crucible with a dimensions of 5 mm in diameter and 6 mm in height. Before heating, the chamber was evacuated for 15 minutes down to a vacuum of 10 Pa. The reaction chamber was then filled with argon. A constant flow rate of 0.3 l/min was then maintained and the gas was led out through the outlet at the lower end of the reaction tube. Initially, the higher temperature limit was chosen as 1923 K, which was found to be high enough over the melting point of pure iron. Further experiments were concentrated on the interested area over the temperature range of 773-1173 K, so the higher temperature limit was set at 1273 K. Two heating rates were employed, namely, 10 and 14 K/min. The weight changes of the sample and the DTA signals were registered on the computer at intervals of 2 seconds, in the case of using a maximum temperature of 1923 K, and 1.2 seconds in the case of using a maximum temperature of 1273 K.

**RESULTS**

**Chemical Analysis**

The chemical analysis results of iron carbide from two different places, Nucor and Wundowie, were summarized in Table II. It is seen that the Nucor sample has higher magnetite content and lower iron carbide content than the Wundowie sample. The Wundowie sample had higher metallization but also a much higher gangue content.

XRD patterns shown in Figure 1 indicate that iron carbide and magnetite are the predominant phases, and iron and wüstite were the minor phases. Nucor’s iron carbide had large proportion of magnetite, and higher ratio of Fe/Fe\(_3\)C than Wundowie carbide. This result is consistent with the chemical analysis. Graphite was also present in the Nucor iron carbide as a minor phase.

**Morphology and Microstructure**
Table II  Chemical analysis of commercial iron carbides

<table>
<thead>
<tr>
<th>Percent item</th>
<th>Iron Carbide</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nucor</td>
<td>Wundowie</td>
<td></td>
</tr>
<tr>
<td>Percent Metallization, %</td>
<td>71.0</td>
<td>77.7</td>
<td></td>
</tr>
<tr>
<td>Total Iron, wt%</td>
<td>84.9</td>
<td>80.7</td>
<td></td>
</tr>
<tr>
<td>Metallic Iron, wt%</td>
<td>9.1</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>Mössbauer Fe₃C, wt%</td>
<td>51.2⁺</td>
<td>59.5</td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄, wt%</td>
<td>31.6</td>
<td>24.8</td>
<td></td>
</tr>
<tr>
<td>Carbon, wt%</td>
<td>3.42</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>0.004</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Gangue, wt%</td>
<td>&lt;1.89</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.25</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.31</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>&lt;0.02</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>&lt;0.05</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>&lt;0.05</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.05</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>&lt;0.05</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;0.02</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt;0.05</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.04</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* This value was calculated from C% theoretically.

Table III  The results of the size analysis for different powders by the Malvern Mastersizer

<table>
<thead>
<tr>
<th>Name of powder</th>
<th>Mean diameter D(v,0.5), μm</th>
<th>Specific surface area, m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucor fine powder</td>
<td>38.63</td>
<td>0.7643</td>
</tr>
<tr>
<td>Nucor Coarse powder</td>
<td>249.48</td>
<td>0.0118</td>
</tr>
<tr>
<td>Wundowie fine powder</td>
<td>23.65</td>
<td>0.4104</td>
</tr>
<tr>
<td>Wundowie Coarse powder</td>
<td>468.92</td>
<td>0.0068</td>
</tr>
</tbody>
</table>
The morphology of the iron carbide powder (Nucor sample) can be seen from the SEM micrograph shown in Fig. 2. The granular solid consists of particles of a wide size range of 10-800 micron. The Nucor iron carbide color varied from dark grey to black, and also has a certain amount of shiny particles visible to the naked eye, while the Wundowie iron carbide appeared dull grey. XRD patterns for shiny particles in the Nucor iron carbide were obtained, as shown in Fig. 3, and it is clear that they contain more iron and iron carbide, and less magnetite when compared with the standard Nucor sample.

An enlarged SEM micrograph for the Wundowie iron carbide particles is shown in Fig. 4. Its morphology presents much undulation and porosity than the Nucor iron carbide. Microscopic examination showed considerable variability in the structures of particles present in the Nucor sample, but quite uniform structure for the Wundowie sample. Presumably, this variability was due to the heterogeneity of the original particles (size, degree of fracturing, presence of multiple phases), the inherently non-uniform sequence of conditions in the fluidized-bed to which each particle was exposed and also the residing time of the materials in the reactor which reflects the degree of conversion to iron carbide.

Fig. 5 presents a typical topochemical pattern of the particle in the Nucor sample with the magnetite phase in the middle and the iron carbide as the outer layer. Examination of a random batch of particles (normally 100 pieces) under microscope showed that approximately 80 percent of the particles had this structure. The rest of the particles, as shown in Fig. 6, were fully converted iron carbide particles of a single phase. The microhardness of these particles vary from 200 to 500 Hv, which is lower than the value for standard cementite phase, as shown in Table I, and might due to the large areas of porosity. A different scenario was found in the Wundowie iron carbide sample which had a rather uniform morphology. Particles with single iron carbide phase can also be found in the Wundowie sample.
with less porous microstructure, compared with the particles in the Nucor sample, as shown in Fig. 5.

Particle Size Distribution

The particle size distribution of Nucor iron carbide powder was determined by sieving. The mean size of 201.32 micron for the Nucor iron carbide was obtained by a tabular calculation method described by Allen. For the finer samples used in the TG and DTA experiments, particle size analysis was determined by using the Malvern Mastersizer. The mean diameter $D[v, 0.5]$ and specific surface area for the four kinds of samples referred to in the TG and DTA experiments were obtained and are listed in Table III.

Thermal Analysis

The results of TGA measurements for the Nucor iron carbide powder with different particle size distribution, namely fine and coarse particles, at constant heating rate (10 K min$^{-1}$) and sample weight (78 mg) in Ar atmosphere, are presented in Fig. 7. The particle size analyses of the powders used in the experiments are given in Table III. It is seen that while both of the reactions started at a temperature of 772 K and with the similar shape of curve, the terminating temperatures of the reactions were found to be 1143 K and 1191 K for the fine and coarse powder respectively. It is obvious that finer powders have the best surface to volume ratio and at any given temperature the extent of reaction is greater than for samples with larger particle size. The smaller the particle size, the greater is the extent to which equilibrium is reached, all other conditions being equal.

Simultaneous TG, DTG and DTA were employed in non-isothermal experiments. The relation between $dn/dt$ and temperature was expressed as DTG curve, which can claim certain advantage over the TG curve in the matter of graphical presentation and it often bear a strong resemblance to DTA curves and permit comparisons to be made. In this investigation the DTG data were calculated from the TG data in an
Fig. 5 Optical micrograph showing typical topochemical pattern of the particle (magnetite in the middle, outer is mainly cementite)

Fig. 6 Optical micrograph showing a fully converted iron carbide particle with highly porous appearance

Fig. 7 Influence of particle size on the reaction for Nucor iron carbide

Fig. 8 TG, DTG and DTA results of Nucor fine sample in Ar gas

Fig. 9 Comparisons of non-isothermal curves between two different samples
interval of 1 minute. The result curves for the Nucor fine powder with the temperature range from 293 to 1923 K at the heating rate of 10 K min⁻¹ are plotted as functions of temperature in Fig. 8.

For the convenience of explanation, the figure has been divided into three parts, A through C, marked by dotted lines. In region A, the starting portion up to 520 K in both TG and DTA curve presents a discontinuity which is due to the deviation of temperature from the linear heating line. Thereafter, up to about 767 K, a slight upward trend shown both in TG and DTA curves is due to the system noise. The DTG curve is nearly horizontal, indicating negligible reactions within the iron carbide particles in this region.

In region B, the TG curve shows a weight loss of 7.6%. It is evident in the DTA curve that there are four endothermic peaks during this stage. The simultaneous TG curve gives more details of the first two peaks when the sample loses its weight sharply and at the second peak at 943 K when the rate of reaction is fastest. This is followed by a slow down at the third peak and after a final rate increase at the fourth peak the weight loss stops, indicating the termination of the reactions within the sample.

In the final region C, there is a consistently slight weight gain as seen in the TG curve, which is also due to the system noise. However, three endothermic peaks at 1201 K, 1667 K and 1827 K are evident as arrow marked in the DTA curve, which would correspond to the phase transformations of iron from α-Fe to γ-Fe, γ-Fe to δ-Fe, and δ-Fe to liquid iron respectively. An XRD pattern of the final sample of the Nucor fine powder after the non-isothermal experiment over temperature range of 293-1873 K in Ar gas indicated that only iron remained. This also to some extent verifies that the weight gain indicated by the TG curve is due to the system noise, not the oxidation reactions. A series of minor endothermic and exothermic peaks in the DTA curve at temperatures from 1380 K to 1640 K exist in this region which could not be explained.

The results of TA experiments for the Nucor fine and the Wundowie fine samples (the particle size analyses of the powders were given in Table III) at constant heating rate (10 K min⁻¹) and sample weight (78 mg) in Ar atmosphere are shown in Fig. 9. It is seen that they show similar shapes in both DTA and DTG curves. However, the DTA curve for the Wundowie sample is rather smooth, because the highly porous character of the sample resulting in its lower thermal conductivity, which is reflected on the response of heat flow in the DTA instrument. Also the TG curve of the Wundowie sample shows no obvious weight change up to 850 K, followed by a three-step weight loss compared with two for the Nucor sample.

**DISCUSSION**

The weight losses recorded in the thermal experiments are thought to be due to reaction between the unreduced iron oxides in the sample and carbon in the sample. The overall reactions can be written as follows:

\[
\begin{align*}
\text{Fe}_3\text{O}_4 + 4\text{Fe}_3\text{C} & \rightarrow 15\text{Fe} + 4\text{CO(g)} \quad (1) \\
\text{FeO} + \text{Fe}_3\text{C} & \rightarrow 4\text{Fe} + \text{CO(g)} \quad (2)
\end{align*}
\]

The thermodynamics of the reactions in the iron carbide powder is complicated by the fact that iron carbide itself is metastable and during heating may decompose into iron and carbon, as per reaction 3 below. In addition, wustite is thermodynamically unstable below 1843 K and would be expected to decompose into iron and magnetite, as per reaction 4.

\[
\begin{align*}
\text{Fe}_3\text{C} & \rightarrow 3\text{Fe} + \text{C} \quad (3) \\
4\text{FeO} & \rightarrow \text{Fe} + \text{Fe}_3\text{O}_4 \quad (4)
\end{align*}
\]

These thermodynamic considerations indicate that during the early stages of heating (below 843 K), there should be little weight loss but some increase in solid carbon and magnetite concentration in the samples. Because these
reactions are solid state and have slow kinetics, the relatively rapid heating of the experiments may have lessened the extent to which these reactions occurred. The solid carbon formed would allow the following reaction to occur:

\[ \text{Fe}_3\text{O}_4 + 4\text{C} \rightarrow 3\text{Fe} + 4\text{CO}(g) \]  

(5)

Reaction 5 is thermodynamically favoured above 997 K and the advent of this reaction corresponds to the endothermic peaks just after 1000 K identified by the DTA measurements for various samples shown in Figures 8, 9 and 10. The earlier peak identified around 943 K is consistent with the reduction of magnetite to wustite, as per reaction 6 below, which is thermodynamically favoured above that temperature.

\[ \text{Fe}_3\text{O}_4 + \text{C} \rightarrow 3\text{FeO} + \text{CO}(g) \]  

(6)

It more difficult to explain the gradual weight gain observed below 767 K, followed by weight loss after that temperature. These observations support the notion that some free oxygen was present in the system and allowed firstly some oxidation of the iron in the system, followed by generation of carbon monoxide and indirect reduction of the iron oxides to take place via the following reaction sequence:

\[ 2\text{C} + \text{O}_2(g) \rightarrow 2\text{CO} (g) \]  

(7)

\[ \text{Fe}_3\text{O}_4 + \text{CO}(g) \rightarrow 3\text{FeO} + \text{CO}_2(g) \]  

(8)

The weight losses recorded between 800 and 900 K supports the notion that some indirect reduction had taken place, as it is known that these reactions can proceed in this temperature range. Analysis of the thermodynamics of the system using Gibbs Energy Minimisation and results from isothermal experiments are the subject of a future paper. Certainly, the complex sequence of reactions taking place in the iron carbide samples makes it difficult to distinguish any separate kinetic effects and only broad generalisations about the rate of carbon monoxide generation can be drawn. It is clear that the rate of CO generation for both iron carbide samples was sensitive to temperature, particle size and heating rate, though the differences in TG and DTA curves found for the two samples are difficult to explain.

Thus weight losses in the samples recorded would correspond to the generation of carbon monoxide from the iron carbide. It is the generation of fine carbon monoxide bubbles from iron carbide that should benefit the removal of nitrogen from molten steel during injection. Thus the onset of carbon monoxide generation from iron carbide is important in the design of injection systems. The observation that the reduction reaction is fastest at 943 K in the non-isothermal experiments suggests that a high injection rate is needed to avoid the reduction reaction occurring during its conveying in the injection system.

**CONCLUSIONS**

A characterization of two iron carbide powders from different places, namely, from Nucor and Wundowie, has shown variations in size, morphology, density and composition. This is probably due to variations in different qualities of raw materials, ore concentrates and natural gas, and conditions employed in the fluidized-bed reactors used to generate the materials. A large portion of particles in the Nucor iron carbide powder has a topochemical profile with a magnetite core surrounded by an iron/iron carbide layer. The Wundowie iron carbide, besides some fully converted iron carbide particles, mainly consists of highly-porous particles with large voids.

Thermal analysis experiments were carried out on the kinetics of reactions between the iron carbide and magnetite in iron carbide powders. Comparisons made in terms of different origin or morphology and particle size of the sample were consistent with the metallographic observations. The results indicate that finer powders have the best surface to volume ratio and at any given temperature the extent of reaction is greater than for samples with larger particle size. The non-
isothermal experiments on the Nucor fine sample showed that reduction reactions occurred at the temperature range of 767 K and 1147 K, and gained the fastest rate at 943 K. Further investigations on the kinetics of CO generation within the particles is recommended, possibly using a constant volume pressure increase (CVPI) technique combined with gas measurement.

ACKNOWLEDGEMENTS

The authors are grateful to BHP Ltd for providing technical assistance and advice during the project, the Australian Research Council for providing funding for the project and the staff of the Department of Materials Engineering at the University of Wollongong for providing technical and administrative support.

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