Factors Influencing Carbon Dissolution from Cokes into Liquid Iron

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In a blast furnace carburisation of iron is one of the most important reactions and must be better understood if the blast furnace is to be made more sustainable. Identifying the key mechanisms governing the rate of carburisation of liquid iron is complicated by the intricate nature of the carbonaceous materials used. In this study two cokes prepared from coals of similar rank, ash yield and carbon crystallite structural parameters were investigated. It is found that the apparent carbon dissolution rate in molten iron at 1823 K for the two cokes differed by over an order of magnitude. Coke 1, $K=1.7 \times 10^{-3} \text{s}^{-1}$, carburised molten iron much faster than Coke 2, $K=1.1 \times 10^{-3} \text{s}^{-1}$ and the difference is attributed to differences in the composition of their mineral matter.

KEY WORDS: carbon dissolution; coke; mineral composition; blast furnace.

1. Introduction

In the blast furnace coke has three major roles:

- Thermal: it is a source of fuel providing the heat required for endothermic reactions and melting of iron and slag.
- Chemical: it produces and regenerates reducing gases to reduce iron oxides and it carburises molten iron.
- Physical: it provides mechanical support to the charge column and a permeable bed below the cohesive zone.

Coke is the most expensive raw material used in the blast furnace ironmaking process and there has always been a demand to decrease its requirement. With the concept of sustainable ironmaking and the pressure to diminish greenhouse gas emissions the need to minimize coke consumption has grown stronger.

One possible approach to making the blast furnace more sustainable and thereby decreasing greenhouse gas emissions is to lower blast furnace operating temperatures. This would lead to high hot metal productivity at lower energy costs and at lower operating temperatures coke usage would also be decreased. This radical approach is currently being explored.11) In light of sustainable ironmaking, the carburisation of iron is a critical reaction since it is largely the metal carbon content that dictates the melting point of the iron. As a result understanding and predicting the carburising performance of cokes is necessary.

The mechanism by which coke carburises iron is an important facet of the ironmaking process but one that is not well understood. This paper reports on the apparent dissolution rate of two Australian cokes, which were made from coals of similar rank and ash yield, in molten iron and the physical and chemical role of their mineral matter on the kinetics of carbon dissolution.

2. Previous Studies

Graphite dissolution has been thoroughly explored but the dissolution of coals, chars, cokes and glassy carbon has been examined only to a lesser degree. Carbon dissolution from graphite is generally thought to be a two-step process:

1. Dissociation of carbon atoms from its crystal site in the graphite into the carbon/melt interface.
2. Mass transfer of carbon atoms through the adjacent boundary layer into the bulk liquid iron.

Studies have shown the second step to be the rate-limiting step, i.e. the process is mass-transfer controlled.2,3) Other investigations4–10) also show that sulfur in molten iron reduces graphite dissolution rates by decreasing the diffusion coefficient of carbon, that is, sulfur reduces the diffusivity of carbon into molten iron.

Non-graphitic carbon dissolution is typically much slower than dissolution of graphitic materials and the effects of sulfur are more significant. This reduction in dissolution rate is attributed to the mineral matter in the non-graphitic carbon source. Orsten and Oeters8) suggest that these minerals inhibit the dissolution process by covering the coke/liquid iron interface, reducing the effective area for carbon dissolution. They conclude that coke ash should be liquid at the dissolution temperature, if dissolution rates are to be high. This, they suggest, is because low ash fusion temperatures allow easy removal of the ash in the form of slag, which results in constant exposure of fresh carbon surface to the hot metal. They suggest that additions of certain oxides, such as calcium oxide (CaO), can decrease the melting temperature of ash and therefore increase dissolution rates.

Results from Gudenu et al.11) Peters et al.12) and...
Mourao et al.\textsuperscript{13}) confirmed that a film of ash/slag appears on the coke surface. They also suggested that the observed decrease in dissolution rate over time was due to the ash layer, which reduced the surface area available for dissolution. Gudenau and co-workers\textsuperscript{11}) also noted that by controlling the ash composition of the coking coal, the carburising ability of cokes could be modified. The presence of iron oxide was found to enhance carburisation rates and other additives such as CaO were found to reduce the dissolution rate of carbon, in contrast to findings from Orsten and Oeters.\textsuperscript{8}) A possible reason for such differences could be due to the method in which the experiments were conducted. For example, Gudenau et al. added pre-determined amounts of ash forming oxides before coking the coal, whereas Orsten and Oeters mixed CaO with coke in order to decrease the fusion temperature of the ash.

Gudenau and Schemmann in their study showed that carburisation was slower for cokes containing high alkali loads. They also impregnated coke samples with 5\% and 10\% K\textsubscript{2}CO\textsubscript{3}-lye and the coke sample with 10\% lye was found to be the slowest carburiser. A layer was observed around the coke sample isolating the coke’s surface from the melt and it was attributed to be the reason for the slow dissolution process.

Recent investigations by Wu et al.\textsuperscript{14}) also illustrate that electrolytic iron interacts differently with natural graphite than with pure graphite. The cause of the observed difference was attributed to the presence of ash in natural graphite, which formed an interfacial layer. This layer restricted contact between natural graphite and the iron droplet and therefore decreased the rate of carbon and sulfur transfer.

Studies conducted by McCarthy et al.\textsuperscript{15}) found iron oxide and silica reduction reactions to be significant at the interface, retarding the accumulation of solute carbon. This indicates that the composition of ash within the coke can considerably alter its carburisation rate and adds complexity to the understanding of the role of ash during carbon dissolution. Ash is not just a physical barrier to carbon dissolution; it actively participates in chemical reactions at the coke/iron interface.

Furthermore, work on coals and chars have shown that atomic structure of the carbon also influences the rate of carbon dissolution. Recent studies\textsuperscript{16,17}) on the dissolution rates of coals and graphite in Fe–S–C melts showed that the rate of carbon dissolution from coal increased with increasing crystallite size, $L_c$. Wu and Sahajwalla\textsuperscript{16}) were able to verify the relationship between the carbon dissolution rate and the structure of coals by quantitatively determining coal structure parameters using the X-ray diffraction technique (XRD). The authors suggested that an increase in $L_c$ values or an improvement in the ordering of carbon atom arrangement can result in an increase in carbon atom dissociation and hence an enhanced effect on carbon dissolution.

The arrangement of carbon atoms in coke, also referred to as the microtexture, is another characteristic used to describe the structural ordering within coke. In general carbon textures of coke fall into two groups when viewed with polarised light\textsuperscript{18,19)}:

- Anisotropic carbon ($>0.2\ \mu$m) is graphitizable and its reflectance varies with the orientation of the plane of polarisation of the incoming light.
- Isotropic carbon ($<0.2\ \mu$m) which is non-graphitizable, amorphous and whose reflectance do not vary with the orientation of the plane of polarisation of the incoming light.

The amount of anisotropic and isotropic carbon in a coke is largely determined by the maceral composition of the precursor coal. There is little information about coke microtexture and its affect on the rate of carbon dissolution in literature.

In summary, mineral matter content, its distribution and atomic structure of the carbon all affect coke dissolution rates, but their relative impact is not well understood. The research focus of this paper is to investigate the effect of the amount and extent of anisotropic carbon and type of mineral matter on carbon dissolution from coke in molten iron.

3. Experimental Method and Materials

Carbon dissolution from 2 different cokes made from Australian coals and synthetic graphite (SG) was investigated using the carburiser cover method in a vacuum induction furnace (Fig. 1) under inert gas (N\textsubscript{2}) protection. The furnace was continuously purged with nitrogen gas and a positive pressure was maintained throughout the experiment.

An iron bath weighing 1.26–1.30 kg was prepared in the induction furnace. The melt temperature was kept at 1 823±10 K and was controlled by a type B thermocouple, which was protected by a disposable alumina sheath. The temperature varied mainly during the loading of the carburiser onto the melt and recovered within the first three minutes of the experiment. The carbonaceous material, 150 g of 1.18–2.36 mm size fraction, was added to the iron bath once the desired temperature of 1 823 K was reached. Molten iron samples were taken directly from the melt via quartz tubing at desired time intervals. Carbon and sulphur contents of the metal samples were determined using infrared absorption spectroscopy.

The compositions of the materials used are shown in Tables 1 and 2. Table 3 lists the chemical composition of the inorganic matter in the two cokes. The major difference in composition is that Coke 1 has a greater amount of iron and less aluminium than Coke 2. Their Ca and K content are comparable.

X-ray diffraction (XRD) technique was used to characterise the atomic structure of both cokes before and after re-

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Schematic diagram of the induction furnace used in carbon dissolution study.}
\end{figure}
action. The degree of ordering of carbon atoms in coke can be characterised by the height of the stack of aromatic layers in the same orientation, \( L_c \). The crystallite size, \( L_c \), was calculated using Scherrer’s equation:

\[
L_c = \frac{0.89 \lambda}{B \cos \theta_B} \quad \text{(1)}
\]

where \( L_c \) is the crystallite size (angstroms, Å), \( \lambda \) is the wavelength of incident X-rays (for cobalt Kα radiation, \( \lambda = 1.7889 \) Å), \( B \) is the angular width at half-maximum intensity of the (002) peak (radians, rad) and \( \theta_B \) is the Bragg angle of the (002) peak (degrees, °).

4. Results and Discussion

Carbon dissolution runs were conducted on two coke samples and synthetic graphite. The first order kinetic equation used to describe the overall process of carbon dissolution is,

\[
\frac{dC_s}{dt} = K(C_s - C_t) \quad \text{...........................(2)}
\]

where \( C_s \) and \( C_t \) represent the saturation solubility and carbon concentration in the iron melt, respectively, at time \( t \). The apparent dissolution rate constant is \( K \) (s\(^{-1}\)). Integrating Eq. (2), we have

\[
\ln \left( \frac{C_s - C_t}{C_s - C_0} \right) = -Kt \quad \text{...........................(3)}
\]

where \( C_0 \) is the initial carbon concentration in the melt. The dissolution rate constant \( K \) can be measured from the negative slope of the plot \( \ln \left( \frac{C_s - C_t}{C_s - C_0} \right) \) versus time. The changes in carbon and sulfur content of the iron bath over time and the determination of \( K \) for the three carbonaceous materials are shown in Fig. 2.

Figure 2 shows clearly that the dissolution rates of the two cokes are different. Coke 1 reacts much faster than Coke 2 and its rate is of the same order of magnitude as synthetic graphite. Inspection of Tables 2 and 3 shows that the difference in reaction rates is not due to ash yield (9.67% in Coke 1 and 12.27% in Coke 2), Ca (2.8% in Coke 1 and 2.7% in Coke 2) or K (0.95% in Coke 1 and 0.55% in Coke 2) content, as they are comparable. Figure 2 also shows that sulfur pick-up follows a similar pattern to carbon dissolution.

The expected percentage of sulfur in the iron, if sulfur is released from the coke only when the carbon is dissolved can be estimated by the relationship

\[
S_{calc} = \frac{S_{incoke}}{C_{incoke}} \times \Delta C \times m_{Fe} \quad \text{...........................(4)}
\]

where \( \Delta C \) is the net amount of carbon in the hot metal and \( m_{Fe} \) is the mass of the iron bath.

The amount of sulfur expected to be dissolved in the iron by this calculation are compared with the actual values in Fig. 3. This Figure indicates that there is a strong connection between sulfur and carbon dissolution.

4.1. Effect of Atomic Structure on Carbon Dissolution from Coke

Figure 4 shows that Coke 1 dissolves in iron much faster than Coke 2 and its rate is of the same order of magnitude as graphite dissolution.\(^{10}\) This is unexpected since other researchers have reported coke dissolution to be rather slow compared to graphite.\(^{13,21}\)

The XRD spectrum of both cokes (Fig. 5) before and after reaction shows a narrowing of the (002) carbon peak, indicating that the ordering of carbon atoms has improved. Recent studies\(^{16,17}\) have reported a link between structural ordering and dissolution rates of non-graphitic carbonaceous materials in liquid iron. The authors suggested that more ordered materials, that is those with higher \( L_c \) values can lead to higher dissolution rates of coals and chars in molten iron. Under current experimental conditions (inert atmosphere and temperature of 1823 K) an improvement in the ordering of carbon atoms is not entirely unexpected as thermal annealing of the cokes can occur. Carbon crystallite size, \( L_c \), of both cokes before and after reaction was determined using Scherrer’s equation\(^{20}\) and is depicted in Fig. 6.
Fig. 2. Change in carbon and sulfur content and \( \ln\left(\frac{C_s}{H_2O} - C_0\right) \) vs. time graphs for a) SG, b) Coke 1 and c) Coke 2.

Fig. 3. Calculated and actual values of sulfur from Cokes 1 and 2.

Fig. 4. Apparent rate constant, \( K \), for the 3 carbonaceous materials at 1550°C.

Fig. 5. XRD spectrum of a) Coke 1 and b) Coke 2.
It is evident that the crystallites are more ordered after the reaction since the $L_c$ values have doubled in comparison to raw cokes. However, there is little difference in $L_c$ between the two cokes: the high dissolution rate of Coke 1 cannot be explained on the basis of crystallite size.

Furthermore, Wu and Sahajwalla\(^\text{10}\) reported the overall dissolution rate constant for natural graphite to be $K = 12.24 \times 10^{-5}$ s\(^{-1}\), which is similar to that of Coke 1, $K = 14.7 \times 10^{-5}$ s\(^{-1}\). One of the main differences in structure between natural graphite and coke is in their crystallite size and therefore the degree of ordering in carbon atom arrangement. From previous work on structure and its influence on the rate of carbon dissolution, natural graphite is expected to have higher $K$ values than cokes in general. However, in this study the $K$ value of Coke 1 is comparable to the $K$ value of natural graphite. Therefore, the difference in crystallite size does not appear to be a dominant factor in influencing the overall carbon dissolution rate, for relatively high ordered materials such as graphite and cokes at high temperatures.

Table 4 illustrates the ash yield and composition of the two carbonaceous materials. There are differences in Al (Coke 1 has 18.9% Al\(_2\)O\(_3\) and natural graphite has 6.17% Al\(_2\)O\(_3\)) content. This suggests that the inorganic component of the coke plays a role in influencing the rate at which carbon dissolves in molten iron. This role seems to be dominant for highly ordered materials such as natural graphite ($L_c = 349 \text{ Å}$)\(^\text{17}\) and cokes ($L_c = 33 \text{ Å}$ for Coke 1 and $L_c = 34 \text{ Å}$ for Coke 2) at high temperatures. The $L_c$ values of these carbonaceous materials at high temperatures are relatively high compared to coals and chars ($7 > L_c < 10 \text{ Å}$).\(^\text{17}\)

Figure 4 also shows that SG dissolves faster than Cokes 1 and 2. This is most likely due to the fact that SG contains very little mineral matter.

### 4.2. Effect of Anisotropic Carbon on Carbon Dissolution from Coke

Structural ordering can also be described in terms of the microtexture of coke, that is to say cokes with higher content of anisotropic carbon are more ordered than those with high content of isotropic carbon.

Petrographic analysis of Cokes 1 and 2 before reaction with molten iron shows that the anisotropic carbon content is similar in both cokes (Fig. 7). The anisotropic carbon content of the two cokes after reaction with molten iron is also depicted in Fig. 7. The anisotropic carbon after reaction is also similar for both cokes, which demonstrates that anisotropic carbon content cannot explain the significant difference in carbon dissolution rates between the cokes.

### 4.3. Effect of Mineral Matter on Carbon Dissolution from Coke

The effect of mineral matter (ash) can be categorised into the following main aspects:
- chemical effect such as in-situ reactions and those at the interface
- physical effect such as the formation of a barrier
- interfacial wettability

### 4.4. Chemical Effect
- Form of Iron

The presence of iron oxide has been reported\(^\text{11}\) to be favourable for carburisation. The chemical composition of the ash analysis is reported in terms of oxides, which can be misleading. Under the experimental conditions used any iron oxide present in coke is readily reduced. It can undergo reduction by solute carbon and therefore reduce net carbon accumulation in the bath and it can also be converted into metallic iron via in-situ reduction. Therefore, it would be difficult under these conditions for iron oxide to be a fluxing agent because the iron is not present as iron oxide.

In addition, electron dispersive X-ray analyses of Coke 1 before reaction identified iron to be in close association with sulfur (Fig. 8). These Fe/S species have atomic ratio similar to pyrrhotite (Fe\(_{1-x}\)S) or troilite (FeS). Furthermore, there was little evidence of oxygen coupled with iron in Coke 1 and Coke 2 appeared to have more iron oxides and less iron sulfides (Fig. 9). On the basis of these results, iron does not act by fluxing the mineral matter, and, if the presence of iron is responsible for the difference in reaction rates, another explanation must be sought.

The form in which iron is in, for example as a Fe/S complex, may be a key in determining the exact role of iron on the kinetics of carbon dissolution. The presence of Fe/S complex may influence chemical reactions occurring at the coke/metal interface.
4.5. Physical Effect

- Iron Content

A closer look at the ash composition (Table 3) of Coke 1 shows that it has an unusually high iron content. The presence of iron oxide has been reported\(^{11}\) to be favourable for carburisation. This study reports that iron oxide acts as a fluxing agent and it is responsible for lowering the ash fusion temperature. Therefore, it is feasible that the layer of ash can be easily removed, continually allowing a fresh surface for carbon dissolution.\(^{11}\) In other words, it has been proposed that the physical barrier formed between the coke/iron interface can be more readily removed for cokes whose ash has low ash fusion temperatures, allowing carbon dissolution to continue. The ash fusion temperature, which was experimentally determined, for Coke 1 (1 443 K) is lower than that of Coke 2 (1 853 K). Therefore, the resultant film of ash in Coke 1 would be liquid at 1 823 K and can be removed from the coke surface exposing a fresh carbon layer for contact with molten iron. However, as mentioned earlier, under these experimental conditions if iron oxide were present it would be rapidly reduced and therefore cannot act as a fluxing agent. Furthermore, the lower ash fusion temperature of Coke 1 could be explained on the basis of differences in alumina content as described in the next paragraph.

Fig. 8. SEM images and EDS analyses of unreacted Coke 1 containing Fe/S complex mineral matter.

Fig. 9. SEM images and EDS analyses of unreacted Coke 2 containing iron oxides.
• Aluminium Oxide, Al₂O₃

Table 3 also shows the aluminium oxide content of Coke 1 to be much lower than Coke 2. Results from Gudenau and co-workers\(^{11}\) showed that increasing the aluminium oxide content significantly retards carbon dissolution from coke. Aluminium oxide is a stable compound and its melting temperature is well above the experimental temperature, thus the liquidus temperature of the interfacial layer would increase as the Al₂O₃ content increases. In other words, cokes with lower aluminium oxide content can also have lower ash fusion temperatures. Therefore the low ash fusion temperature argument can also be explained on the basis of Coke 1 having a lower amount of Al₂O₃ than Coke 2.

4.6. Interfacial Phenomena

As a result of the physical and chemical interactions occurring between coke, mineral matter and molten iron, the wettability of the coke would change with time. The removal of carbon over time at the interface leaves behind an interface that is enriched with ash. This enriched ash interface can physically limit the contact between carbon and iron if the wetting between the iron and ash is not good. Changing the wettability of the coke would change the contact surface area between iron and coke and this may therefore influence the dissolution rate. The difference in chemical compositions of Cokes 1 and 2 may lead to variations in the interfacial layer that is formed in the two cases. Hence, it is not unreasonable to expect differences in wettability between the two cokes. Sulfur-containing solids are wetted by iron better than aluminium oxide containing solids: the contact angles in the CaS–Fe system and the Al₂O₃–Fe system at 1873 K under argon protection are 87° and 122°, respectively.\(^{22}\) In addition, work conducted by Zhao and Sahajwalla\(^{23}\) on the wetting of graphite/alumina mixtures by iron, show that an increase in Al₂O₃ content increases the contact angle and decreases wetting by iron. Therefore, S and Al₂O₃ in the coke’s mineral matter content can also influence the wettability of coke at the interface.

From Table 2 and 3, Coke 1 contains less Al₂O₃ and more sulfur than Coke 2. Figures 2(b) and 2(c) show that the metal sulfur content of Coke 1 after 5 minutes is 0.05 wt% whereas for Coke 2 it is 0.02 wt%. The increased level of sulfur in the metal can lower the surface tension and thereby lead to an improved interfacial wetting. This could be a factor contributing to the enhanced rate of carburisation in the case of Coke 1.

The above discussion highlights that the nature of the ash constituents plays a dominant role on the overall rate of carbon dissolution in cokes. In addition, comparison of K values from SG and the two cokes shows that the apparent dissolution rate constant for SG is higher than both cokes. This is most likely due to lower levels of ash in SG.

Further research is underway to investigate the interfacial phenomena occurring at the coke/iron interface and its effect on carbon dissolution rates.

5. Conclusions

From the kinetic study of 2 Australian cokes, which were produced from coals of similar rank and ash yield, the main conclusions are:

1. There is significant difference in the dissolution rates of the different cokes.
2. Dissolution of sulfur seems to be associated with carbon dissolution.
3. There is no obvious effect of crystallite size and anisotropic carbon content on the rate of carbon dissolution.
4. Ash composition is a dominant factor that influences the rate of carbon dissolution. Both the physical and chemical effects of mineral matter need to be considered in any proposed explanation for the variation in carburisation rates.
5. Iron and aluminium content in coke, and in particular their mineralogy, play a key role in influencing the rate of carbon dissolution.

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