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Wettability of Carbonaceous Materials with Molten Iron at 1550°C

R. Khanna, I. Mansuri and V. Sahajwalla

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http://dx.doi.org/10.5772/61198

Abstract

In the direct iron smelting process, interfacial reactions of carbonaceous materials with molten iron are among some of the key factors that dictate the rate of carbon transfer into molten iron and establish a carbon concentrated melt to reduce iron oxide in the slag phase. Detailed wettability investigations on a range of carbonaceous materials, e.g. synthetic graphite, natural graphite, coke, coal-chars, coke-polymer blends, waste plastics in contact with molten iron at 1550°C were carried out using the sessile drop method. Experimental results on dynamic contact angles are presented in this chapter and are discussed in terms of the basic characteristics of carbons and the changing composition of the interfacial region as a function of time.

The influence of carbon and sulfur content in Fe-C-S melts on the wettability of synthetic graphite was investigated. The initial melt carbon content was in the range of 0.13 to 2.24 wt %, and the melt sulfur content was in the range of 0.05 to 0.37 wt %. It was found that the contact of solid graphite with Fe-C-S melts resulted in a non-equilibrium reactive wetting. It involved the transfer of carbon from the solid to the liquid and iron transfer from the liquid to the solid. The Fe-C-S melts exhibited relatively poor wetting in the absence of such a material exchange.

The wetting of natural graphite, which contained 8.8 pct ash, by iron was investigated to establish a fundamental understanding of the influence of ash on interactions between graphite and iron. It was found that the formation of an ash interfacial layer between the carbonaceous material and liquid iron had a strong influence on the mass transfer and interfacial reaction.

Wetting investigations of pure liquid iron with three types of metallurgical cokes at 1550°C showed a non-wetting behaviour for all cokes with contact angles ranging from 123° – 126° initially, which marginally decreased to 109°-114° after 60 minutes.
of contact. The slight decrease in contact angles was attributed to the transfer of carbon from coke to liquid iron, which then led to a lower the interfacial tension.

The wettability of four non-graphitic coal-chars with electrolytic pure iron was investigated at 1550°C. The ash concentration in chars ranged between 9.04 and 12.61 wt %, with alumina and silica as predominant ash components. The initial contact angles ranged between 106° and 137°, the contact angles for all coal-chars were quite similar after 60 minutes of contact (105 - 110°). While no well-defined correlations could be observed between the initial char structure and ash concentration/composition and contact angles in the initial stages of contact, the contact angles over extended periods were significantly affected by the presence of reaction products and impurity deposits in the interfacial region.

Keywords: Carbonaceous materials, molten iron, wettability, contact angles

1. Introduction

Ironmaking is one of the largest consumers of carbon fuels in the world, with an annual energy consumption of 24 EJ (x 10¹⁸ J) and 69% of the world’s total energy consumption in iron/steelmaking industry [1]. Conventional ironmaking involves temperatures of more than 1500°C, leading to high-energy consumption. It is also dependent upon high quality coking coal, and cannot use low-grade waste materials such as coal fines. To lower both the pollution and carbon emissions, the energy consumption levels need to be lowered and this can be achieved by lowering the temperature of ironmaking. Previous attempts to lower the temperatures have focused on macro-scale reactions. There have been attempts to develop a lower-temperature ironmaking process to reduce energy requirements and emissions by replacing coke with coal fines; but what have been predominantly iron oxide reduction and industry-oriented experiments, have encountered crucial issues of operational stability and low-temperature carburization.

Mechanisms for liquid iron carburization were extensively investigated in a previous study from our group [2] and the results showed a close relationship with composition of inorganic materials, carbon structure, and temperature. However, solid state carburization is rather complex due to the combination of gas phase carburization reaction and solid state diffusion of carbon [3, 4]. Due to difficulties associated with measuring contact angles with fine powders, very limited information is currently available on the wettability of non-graphitic carbons, such as coal-chars, and the role of carbon type and ash composition is not well determined.

In the direct iron smelting process, interfacial reactions of carbonaceous materials with molten iron are among some of the key factors that dictate the rate of carbon transfer into molten iron and establish a carbon concentrated melt to reduce iron oxide in the slag phase. Basic parameters such as wettability, fixed carbon, ash content/composition, and crystalline order of the carburizing material influence the dissolution kinetics of carbon [5, 6]. Various metal oxides
present as ash impurities can also form a viscous layer in the interfacial region affecting wettability and may act as a physical barrier for the transfer of carbon. An understanding of wettability and associated interfacial phenomena is required to establish carburizing fundamentals of various carbonaceous materials. The interfacial phenomena between carbonaceous materials and molten iron is very important due to the extensive use of these materials in iron and steelmaking.

Wu and Sahajwalla provided an alternative explanation for the initial decrease in the contact angle for Fe-C-S melts on graphite followed by a recovery to the equilibrium value [7]. They postulated that the initial decrease was due to the diffusion of carbon and sulfur atoms to the interfacial layer resulting in a reduction in the interfacial tension between the solid and the liquid. Once the diffusing species reduced the chemical potential difference between the solid and the liquid to negligible levels, the Van der Waals forces begin to dominate the wettability. This results in the contact angle approaching its equilibrium value.

The presence of surface-active elements at the interface can affect the interfacial energy. Surface activity is defined as the magnitude of change in surface tension brought about by the addition of a unit quantity of the species. The ultimate surface activity of a surface-active species in a binary system generally decreases with increasing temperature. Additions of more than one solute to a system complicate the determination of surface activity. The compounded results cannot be predicted from the individual contributions. For example, carbon, a non-surface active element, increases the activity coefficient of the dissolved sulfur in liquid iron, lowers the surface tension of Fe-C-S solutions thereby enhancing the surface concentrations of sulfur.

In an atomistic computer simulation study on the Fe-C-S system, S and C were found to mutually displace each other. Carbon-rich regions were depleted of sulfur and vice versa [8].

Detailed wettability investigations on a range of carbonaceous materials, e.g., synthetic graphite, natural graphite, coke, coal-chars, coke-polymer blends, and waste plastics, in contact with molten iron at 1550°C were carried out using the sessile drop method. Experimental results on dynamic contact angles are presented in this chapter and are discussed in terms of the basic characteristics of carbons and the changing composition of the interfacial region as a function of time. The systems of interest in this study is rather complex: along with a heterogeneous composition, the carbonaceous materials contain non-graphitic carbon and ash minerals; the liquid metal typically contains carbon, sulfur, and quite a few trace elements. In combination, these can result in a number of reactions occurring in the interfacial region, which could have significant influence on the wettability of the system.

2. Experimental

The wettability of carbonaceous materials and Fe-C-S system was investigated in a laboratory-scale, horizontal tube resistance furnace using the sessile drop approach. The carbonaceous materials formed into cylindrical substrates (25 mm diameter, 3–4 mm height) and compressed under 7 tonne pressure (for approximately 1 minute) using a hydraulic press (ENERPAC, Australia®). The weight of the metal used was ~0.70 g of electrolytic-grade iron and Fe-C-S
alloys, respectively. The static nature of the droplet in the sessile drop arrangement helps to preserve the interfacial layer that forms between the iron and carbonaceous materials, allowing a detailed investigation of the interface. Apart from Marangoni flow, there is minimal flow within the liquid iron droplet in the sessile drop method.

A schematic diagram of the experimental arrangement is shown in Fig. 1. The furnace tube had an inside diameter of 50 mm. Initially, the metal/carbon assembly was held on a specimen holder, which could be pushed to the center of the hot zone in the furnace with the help of a graphite rod. The metal/carbon assembly was held in the cold zone of the furnace until the desired temperature (1550°C) was attained. The assembly was then inserted into the hot zone; this eliminated any reaction that could occur at lower temperatures and possibly influence the phenomena to be studied at the temperature of interest. The melting of iron marked the beginning of contact time. The furnace tube was purged with argon throughout the duration of the experiment with a flow rate of 0.5 L/min.

The wettability behavior of the metal/carbon system was investigated using a closely controlled and visually monitored sessile drop technique. A high-quality, high-resolution charge-coupled device (CCD) camera fitted with an IRIS lens was used to capture the live in-situ phenomena in the furnace. The output from the camera was channeled to a video cassette recorder (VCR) and a television (TV) monitor to record the entire process as a function of time. This allows specific images, displaying the contact between the metal and carbonaceous material, to be captured from the videotape, as a function of time, into a computer using a frame grabber. A time-date generator is used in the system to display the duration of the process. For a better understanding of reaction dynamics, contact angles were recorded up to 2 hours in most cases. Fig. 2 shows a representative image of molten iron droplet during melting in the horizontal tube furnace.

Specially designed computer software was used to determine the contact angle from the captured images, on the basis of a curve-fitting exercise. The contact angle between the iron
The contact angle was measured by using computer image analysis software based on a curve-fitting algorithm. The working principle of this algorithm is detailed in the work conducted by [7] and is shown in Fig. 2. Typical accuracy of contact angle measurements was within ± 5%.

3. Wettability and interfacial phenomena

Wettability investigations were carried out on a number of carbonaceous materials in contact with molten iron at 1550°C. Detailed results are presented in this section.

3.1. Synthetic and natural graphite

A number of researchers have investigated the wettability between graphite and pure iron, graphite and Fe-C alloys at temperatures of 1300–1550°C under atmospheres of helium, argon and hydrogen gases and in vacuum. These studies have shown that pure iron showed good wetting with graphite at high temperatures under these conditions. During sessile drop experiments of iron with graphite, it was observed that in the initial stages, when the iron had melted completely, the carbon content had reached 4.23%; and in the final stages, it had reached the saturation carbon level of 5.62%. The contact angle changed from 64° at the initial state to 38° in final stages when the carbon content had reached saturation.

Lower contact angles in C/Fe interaction have been explained through the lowering of interfacial tension between the two phases due to the mass transport across the interface. The low value of the contact angle was maintained even when the carbon transport rate slowed down at higher carbon content in the liquid droplet during the later period of carbon had dissolution reaction [9, 10]. Thus for the sessile drop experiment, the reaction area was
estimated reasonably well by the lower value of the contact angle. Some experimental results are listed in Table 1.

Sun et al. [13] found that the contact angle of iron on carbon with 0% initial carbon was 59° at 1500 °C, while that of a sample with 4.8 wt% carbon was 118°. It was considered that the contact angle for a low carbon sample is very small, because a lower interfacial tension exists during
the rapid initial carbon pickup reaction occurring at the metal-graphite interface. This initial rapid carbon pickup is considered to occur during and immediately after melting. Once the interfacial area extends during the initial carbon pickup reaction, it cannot recover to the shape where a higher carbon content sample was used, even though carbon content reaches the saturation level. These studies showed that pure iron had good wetting with graphite at high temperatures under vacuum, helium and hydrogen and argon gases [7, 11].

<table>
<thead>
<tr>
<th>Metal</th>
<th>Substrate</th>
<th>Atmosphere</th>
<th>T (°C)</th>
<th>θ (°)</th>
<th>Reference</th>
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<tbody>
<tr>
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<td>H₂</td>
<td>1550</td>
<td>37</td>
<td>[11]</td>
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<td>107</td>
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<tr>
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<td>66</td>
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<td>[7]</td>
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<td>Argon</td>
<td>1600</td>
<td>72-54-61</td>
<td>[7]</td>
</tr>
</tbody>
</table>

Table 1. Some experimental results on the wettability of synthetic graphite.

Wu and Sahajwalla [7] investigated the dynamic wetting behavior of Fe-C-S melts with graphite substrate using a sessile drop technique by focusing on the influence of melt carbon and sulfur concentration on the wettability at 1600°C. The wettability between the Fe-C-S melt and solid graphite has been presented in terms of the changes in contact angles with time (Fig. 4).

Figure 4. The variation of contact angles as a function of time for molten Fe-S-C and graphite system.

From Fig. 4, in the initial state (within ~8 seconds of contact), the system is observed to be non-wetting (~100°). Thereafter, this system becomes wetting (~60°) with a considerable decrease
in the contact angles (in the time period ~8 to 90 seconds). The contact angles were observed to stabilize at ~60° for the rest of the experimental time. The changes in contact angles in this system were attributed to carbon and iron inter-diffusing into the solid graphite and the liquid iron.

Wu et al. [14] investigated the wetting behavior of natural graphite and liquid iron system using the sessile drop technique and the results are shown in Fig. 5. The contact angles of this system decreased from ~100° to become wetting within the first 10 seconds (~60°). Thereafter, it became non-wetting with the contact angles sharply increasing to stabilize at ~100° within 100 seconds. This dynamic wetting behavior of iron and natural graphite is very different from the behavior of molten Fe-C-S and graphite systems; the deposition of ash oxides at the interface played a strong role in this phenomena.

Figure 5. The variation in the contact angles as a function of time for molten iron on natural graphite substrate.

3.2. Coal chars

Raw coals were crushed in a jaw crushe and vibrating grinder, and wet sieved and the resulting size graded samples were dried in an oven prior to char making. The chars were produced from raw coals in a drop-tube furnace in an atmosphere of 23 % O₂ in N₂ at a temperature of 1200 °C.

The wettability for four chars was determined using the sessile drop approach and the contact angles were measured. Chars 1 and 2 had a very high initial contact angle of 145° and 140° respectively, which decreased to ~110° after 60 minutes of contact. While the contact angle for Char 1 showed a gradual decline with time, the contact angles for Char 2 showed a sharp reduction to 110° after 2 minutes of contact and then fluctuated around that value over long times of contact. Chars 3 and 4 had somewhat lower initial contact angles, 115° and 120° respectively, but these showed no improvement with time. Following a trend contrary to Chars 1 and 2, these chars did not show a sharp initial decline; there were only marginal fluctuations in contact angles as a function of time. After 60 minutes of contact, the contact angles for all four chars were quite similar ranging between 105–110°.
Only a marginal improvement in wettability (decrease in contact angles) was observed as a function of time. The authors identified the factors influencing the wettability as: transfer of carbon and sulfur across the metal/carbon interface, the formation of Al₂O₃ and CaS complexes at the interface and the reduction of reducible oxides, such as SiO₂ and Fe₂O₃, and the transfer of Si into the liquid metal.

3.3. Metallurgical coke

An experimental investigation of the wetting behavior of pure liquid iron with three types of metallurgical coke at 1550°C was conducted by Cham et al [15]. It was observed that all cokes showed a non-wetting behavior with contact angles ranging from 123°–126° initially, which marginally decreased to 109°–114° after 60 minutes of contact. It was concluded that the slight decrease in contact angles was due to the transfer of carbon from coke to liquid iron, which then decreased the interfacial tension. On the other hand, the effects of sulfur, ash content and composition and carbon structure on the wettability could not be observed in this study.

The wetting images of molten steel droplet on coke after 60 minutes of reactions are shown in Fig. 6. It can be seen that the liquid steel droplet showed a non-wetting behavior with the coke (contact angle 129°) initially and the value increased slightly within the first few minutes. A very small change was observed throughout the experimental run with the contact angle reaching 128° after 60 mins of contact.

![Wetting images of steel droplet after reaction with coke for 60 minutes at 1550°C.](image)

3.4. Metallurgical coke/Bakelite blends

A number of polymers and metallurgical coke were blended in three different ratios: Blend 1, Blend 2, and Blend 3. These were labelled as BK1, BK2, BK3; H1, H2, H3; and P1, P2, P3 for
Blends 1, 2 and 3 of Bakelite/Coke, HDPE/Coke, and PET/Coke, respectively. Fig. 7 represents the blending ratios used in these blends.

![Blending Ratios](image)

**Figure 7.** Relative proportions between the plastics and metallurgical coke in the polymer/coke blends.

The raw polymer/coke blends were combusted in a drop tube furnace (DTF) at 1200°C under an atmosphere of 80% nitrogen and 20% oxygen with a gas flow rate of 1.0 L/min, and the chars obtained were used for steel/carbon interaction investigations. The devolatilization was carried out to simulate the real process in Electric Arc Furnace (EAF) steelmaking. In EAF steelmaking process, the carbonaceous materials are injected into the furnace and these undergo partial combustion before coming into contact the molten steel.

![Wetting Images](image)

**Figure 8.** Wetting images of steel droplet after reaction with blend BK1 for 60 minutes at 1550°C.
Wetting results showed variations in contact angle between the Bakelite/coke blends. A general improvement in the wettability of the liquid steel with Bakelite/coke blends was observed as compared to wettability with coke alone.

The wetting images of molten steel droplet on blends BK1, BK2, and BK3 and corresponding contact angles after 60 minutes of reactions are shown in Figs. 8–13, respectively.

Figure 9. Variation of contact angles of steel droplet with blend BK1 and coke substrates at 1550°C.

Figure 10. Wetting images of steel droplet after reaction with blend BK2 for 60 minutes at 1550°C.
From these figures, it can be seen that the liquid steel droplet showed a non-wetting behavior with the coke (contact angle 129°) initially and the value increased slightly within the first few minutes. Bakelite containing blends were also found to exhibit non-wetting behavior with liquid steel. The liquid steel droplet exhibited better wetting with blend BK1 substrates with the measured contact angles being approximately 10° lower than that seen with coke alone. The initial contact angle was 118° that increased to 121° after 60 minutes of reaction. In the case of blend BK2, the initial contact angle was 123° that decreased to 120° after 15 minutes and

![Figure 11. Variation of contact angles of steel droplet with blend BK2 and coke substrates at 1550°C.](image)

![Figure 12. Wetting images of steel droplet after reaction with blend BK3 for 60 minutes at 1550°C.](image)
then increased to almost 139° after 60 minutes. In the case of BK3, the initial contact angle was 131° that initially decreased to 120° after 25 minutes and then increased to 129° after 60 minutes.

The wetting behavior observed in the case of blends BK2 and BK3 was similar to that observed in natural graphite and liquid iron system by Wu et al. [14]. These authors investigated the wetting behavior of natural graphite with liquid iron at 1600°C using the sessile drop technique. They observed a decrease in contact angles (from ~100° to ~60°) along with a rapid increase in the carbon content in the metal droplet within the first 10 seconds of reaction. Thereafter, the melt carbon content was observed to slightly decrease and the contact angles were observed to increase from ~60° to ~100° within approximately 2 minutes of contact and then stabilize for the rest of the reaction times. Wu et al. [14] explained that the decrease in contact angles within the first 10 seconds was due to a decrease in the interfacial tension due to the dissolution of carbon into the melt. Thereafter, the contact angles increased because of a slowing down in carbon dissolution since the formation of ash layer at the metal/carbon interface became significant (interfacial blockage and consumption of solute carbon by reducible oxides). The carbon dissolution into the metal droplet and the ash deposits in the interfacial region were also expected to influence the wetting behavior between molten steel and Bakelite/coke blends.

3.5. Bakelite char

Wettability investigation was carried out using Bakelite char substrate and molten iron. Video images and the measured contact angles between the substrate and molten iron is shown in Figs. 14 and 15. A non-wetting behavior (contact angle > 90°) was observed for Bakelite char with liquid iron. Initial contact angle (at 0 minutes) between Bakelite char substrate was found to be 125.7° and decreased to 122.4° after 1 minute of reaction time. Not much change in contact angle was observed at longer times and angles remained more or less constant later on.
3.6. Waste CD char

A wettability study was carried out using waste CD char substrate and molten iron. The contact angle between the substrate and molten iron was measured and is shown in Figs. 16 and 17.
During initial contact from 0 to 10 seconds, a small decrease in contact angle was observed from 79° to 70°, possibly due to the transfer of carbon and also due to a change in interfacial energy due to interaction between char and molten iron. Wu et al. had observed a similar behavior while using graphite as a carbon source. During later periods, an increase was observed in contact angles that reached 100° after 3 minutes and stabilized at 105° after 15 minutes thereby indicating a much poorer wetting with the carbon level in molten iron approaching saturation. This result points to a much lower driving force for carbon dissolution.

Figure 16. The wetting behavior of waste CD char substrate in contact with molten iron as function of time.

Figure 17. Contact angle as a function of time between iron and waste CD char substrate.
4. Concluding remarks

Detailed results have been reported on the wettability of a wide range of carbonaceous materials with liquid iron at 1550°C and important fundamental data on contact angles have been provided. This study has identified important drivers in the form of interfacial reactions; the evidence suggests that the deposition of reaction products in the interfacial region strongly affected the wettability and therefore the contact area between carbons and liquid iron. Main findings of this investigation are:

The effect of structure on the initial wettability of carbons were found to be marginal, with no well-defined trends observed with $L_c$ values. Wide variations were observed in contact angles for chars possessing very similar $L_c$ values. Due to the likelihood of structure evolution and changes in particle morphologies, no comments however can be made regarding the influence of structure on contact angles over prolonged periods of contact.

While no correlations were observed between initial contact angles and ash concentration/composition, final contact angles were significantly affected by the presence of reaction products and impurity deposits in the interfacial region. Aluminum, calcium, sulfur, oxygen, and iron were detected in the interfacial layer. Small concentrations of magnesium and silicon were also detected indicating the partial presence of the parent ash. The presence of ash impurities and the nature of the interfacial layer play a very important role in affecting the wetting behavior, as it is this material that the liquid iron is in quasi-equilibrium with.

It is quite likely that combinations of several reactions occur simultaneously to dictate the wetting behavior. Reactions that could occur and subsequently influence the contact angles are: the formation of an enriched interfacial layer containing calcium, sulfur, and alumina; transfer of carbon and sulfur by mass transport across the interface; and reduction of reducible oxides such as silica and iron oxides, and possible transfer of these elements into liquid iron.

The mass transfer between solid carbons and iron melts was observed to strongly enhance the wetting phenomena and lowered contact angles. The reduction of system free energy corresponding to the mass transfer reactions was found to influence the formation of the interface region and resulted in the progressive spreading of the wetting line. The composition and thickness of the carbon/iron interfacial layer was dependent on the intensity of mass transfer across the interface. The resulting change in the interfacial energy $\gamma_{ls}$ was a strong function of mass transfer, and was found to vary with the time of contact. The influence of carbon content on the wetting phenomena could only be seen in the initial stages, whereas the influence of sulfur on the wettability was found when the system approached equilibrium.

Acknowledgements

This work was supported by the Australian Research Council (ARC) funds. We gratefully acknowledge their financial contribution. We thank Ikram-ul-Haq and Somyote Kongkarat for some of the experimental work reported in this article.
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http://dx.doi.org/10.5772/61198

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