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B. J. Monaghan

University of Wollongong, monaghan@uow.edu.au

M. Chapman

University of Wollongong

S. Nightingale

University of Wollongong

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The Wetting of Liquid Iron Carbon on Aluminate Minerals Formed During Coke Dissolution in Iron

Brian J. Monaghan¹, Michael W. Chapman¹ and Sharon A. Nightingale¹
¹Pyrometallurgical Research Group, University of Wollongong, Wollongong, NSW 2522, Australia

Abstract: From previous studies by the authors on the effects of mineral layer formation at coke-iron boundary during coke dissolution it was found that the composition and morphology of the layer had a profound affect on the kinetics of reaction. Moreover it was found that the layer was primarily composed of calcium aluminate's that over time (0-120 minutes) became progressively enriched with calcium. The minerals identified in the layer were alumina, CA6, CA2 and CA. Given that coke dissolution in iron is a heterogeneous reaction it can be expected that the wetting of iron on these minerals would have a significant effect on the rate of carbon transfer to the iron. In this paper the results of investigation of wetting of iron on alumina, CA6, CA2 and CA over the temperature range 1450 to 1550°C are presented. Preliminary analysis indicate that the effects of temperature were not as significant as the type of mineral in the layer and that the contact angle decreased with increasing calcium content of this mineral. These results are broadly consistent with experimental observations of how the mineral layer adheres to the iron substrate in the aforementioned coke dissolution study.

Key words: wetting; coke dissolution; coke mineralogy; liquid iron

Coke dissolution in liquid iron is a key reaction in a blast furnace [1]. As coke is dissolved in the iron, there is potential for a mineral layer to form at the coke-iron interface and inhibit further dissolution. In a study by Chapman et al [2] focussed on understanding the effects of mineral formation on coke dissolution it was found that the composition and morphology of the mineral layer formed on dissolution had a profound affect on the kinetics of reaction. Moreover it was found that the layer was primarily calcium aluminate based and that over time (0-120 minutes) became progressively enriched with calcium. The minerals identified in the layer were alumina, CA6 ($\text{CaO} \cdot 6\text{Al}_2\text{O}_3$), CA2 ($\text{CaO} \cdot 2\text{Al}_2\text{O}_3$) and CA ($\text{CaO} \cdot \text{Al}_2\text{O}_3$). The appearance of the CA phase coincided with a significant decrease in the rate of carbon transfer to iron. The CA phase is a dense block-like structure and its appearance caused a densification of the mineral layer. The CA6 and CA2 formed relatively porous structures. It was argued [2] that this densification due to the change in mineral structure caused the decrease in the coke dissolution kinetics. These findings were broadly consistent with what had been previously reported in the literature [3,4,5] but the information on the mineral structures formed was new and warranted further investigation.

For carbon to transfer directly from the coke to the liquid iron in the presence of mineral layer at the interface then channels within the layer must be considered. Metal penetration through these channels can be described by a capillary model as given in equation 1[6]

$$z_e = -\frac{2\sigma \cos \theta}{r\rho g} \quad (1)$$

where z_e , the penetration depth, is a function of the surface tension (σ) of the metal, the radius (r) of the

channel, the contact angle (θ) of the iron on the mineral layer, the density (ρ) of liquid iron and gravity (g). When z_e is greater than the mineral layer thickness then direct transfer can occur. There is the possibility that the mineral layer can have a thickness greater than z_e and therefore prohibit direct transfer of carbon from the coke to the iron. Under such circumstances it would be expected that the rate of carbon transfer would be relatively slow as it would rely on a gas phase or reagent transfer through the mineral layer structure for carbon transfer to occur. If the interfacial characteristics of the CA phase in contact with liquid iron resulted in a small z_e relative to the mineral layer thickness, then this could be considered another possible explanation of why the coke dissolution rate slows on appearance CA in the layer. In order to assess this possibility, changes in θ of the liquid iron-mineral layer system as a result of changes in the layers mineralogy were studied and the results are reported in this paper.

1 Experimental Method

The sessile drop technique was used to measure the contact angle between iron melts and alumina, CA6, CA2 and CA mineral phases using a Sony HD 6.1MP Handycam camera at temperatures at 1450, 1500 and 1550°C. The procedure consisted of heating $0.1 \pm 0.05\text{g}$ of iron alloy on a substrate made from the above minerals in a dried high purity argon atmosphere of flow rate 0.25l/min. Using captured video images, the contact angle, the droplet diameter, droplet height and contact radius were made using the image analysis software package ImageJ with the drop snake plug-in. This size of droplet was selected to minimise gravitational effects and maximise image quality and great care

was taken to ensure that the substrate was level in the furnace.

The Fe-5%[C] melt composition used in the experimental programme is given in Table 1.

Table 1 The Fe-5%[C] melt composition

[C]	[S]	[Si]	[Ti]	[Mn]	[Ca]	[Al]
5.01	<0.003	0.01	<0.002	<0.01	<1ppm	<0.003

The substrates were made from high purity alumina and CaCO₃ reagents and pressed and sintered in the laboratory. The substrate phases were confirmed using XRD and polished to a 1µm diamond finish prior to use in the sessile drop experiments.

Bulk density and porosity measurements of the substrates were measured in accordance with ISO 5017[7] These values are given in Table 2.

Table 2 Density and porosity of the substrates

Substrate	Bulk Density, g/cm ³	% Porosity
Al ₂ O ₃	2.99	23.4
CA6	2.67	20.9
CA2	2.18	25.0
CA	2.68	10.2

A typical sessile drop image used in the θ measurement is given in Fig. 1.

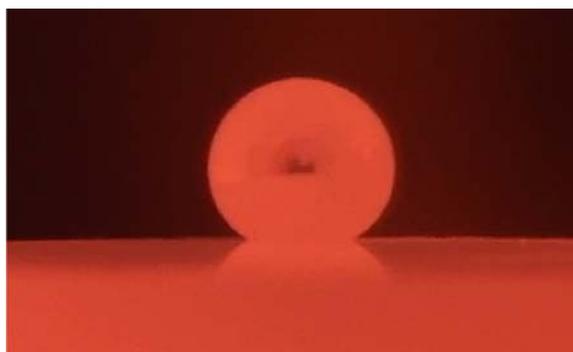


Fig. 1 Captured image of a Fe-5%[C] melt on an alumina substrate at 1500°C. The mass of the droplet is 0.1g.

2 Results/Discussion

The contact angles for Fe-5%[C] melt on different substrates are given in Fig.2. From this figure it can be seen that the contact angle decreases as alumina→CA6→CA2→CA. The reported contact angles are an average of the individual angles measured at approximately 5 minute intervals over a

30 minute period. Each combination of substrate and melt was repeated 2 or 4 times. The majority of the measurements had a scatter of less than ±5% around the mean and were time independent. The 1550°C Fe-5%[C] melt on alumina experiments were an exception. In these experiments the contact angle tended to decrease with increasing experimental time. The decreasing contact angle indicates a dynamic wetting system. Inspection of these samples after the experimental runs indicated some reaction with the melt and alumina substrate.

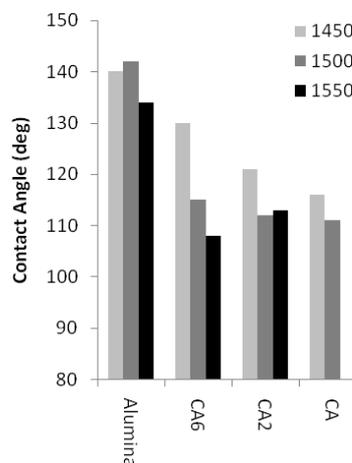


Fig. 2 Contact angle measurements of Fe-5%[C] melt on different substrates at 1450, 1500 and 1550°C.

The contact angles between the iron drops and the alumina substrates measured in this study are consistent with the available literature. Values for the contact angle between pure iron and pure iron-carbon alloys and alumina are reported to be in the range of 141° to 132° in Keene's review of the system [8]. No published data was found on calcium aluminates in contact with liquid iron to make a direct comparison.

2.1 Potential metal-substrate interactions

At 1550°C, the apparent time dependence of the contact angle in the Fe-5%[C] melt on an alumina substrate, indicates that there is a reaction occurring between the substrate and the melt. The most likely reaction would be that involving alumina and the solute carbon in the melt. Though such a reaction is not normally considered thermodynamically favoured other workers have made similar observations with iron and alumina at this temperature.

In surface tension studies Kozakevitch and Urbain [9] observed reaction between high carbon alloys and alumina at 1550°C, and suggested that

bubbles of CO and Al₂O₃ were formed at the interface. They also noted that the intensity of this reaction was decreased at 1500°C. Nizhenko and Floka [10] observed bubbles at the melt interface of Fe-C melts of eutectic composition and alumina at 1600°C noting a significant increase of the aluminium content of the melt. These studies lead to Keene including the warning “surface tension data on the Fe-C system should be treated with caution, particularly in circumstances where metal/support reactions can arise (eg high carbon levels, high temperature) which could lead to changes in melt composition and to non-equilibrium conditions” in his review of data for the surface tension of iron and its binary alloys [11].

2.2 Effect of temperature on contact angle

Within the Fe-C melt results, temperature is observed to have a slight effect on the wetting behaviour of the melt on the alumina and calcium aluminate substrates. The increased temperature results in a slight lowering of the contact angle, indicating an increase in the wetting of the substrate. This is consistent with the expected decrease in the surface tension of the melt with increased temperature, however it may also represent the increased substrate interaction with the droplet.

2.3 Effect of substrate on contact angle

The different calcium aluminates display different wetting behaviour from alumina and each other. It was found that the contact angle decreased (the wetting increased) as the proportion of lime (CaO) in the substrate was increased. This trend is can be seen in Fig. 3 for the 5% [C] melt, while the available data for iron wetting on Al₂O₃ and CaO [8] are included as vertical bars spanning the reported range of contact angles.

2.4 Contact angle, wetting and coke dissolution in iron

For all other things being equal, a lower contact angle (greater wetting) would result in a greater depth of penetration of the mineral layer (see equation 1). Therefore from the contact angles measured there is a greater potential for the melt to penetrate the mineral layer formed on coke dissolution as CA₆→CA₂→CA. If this was the sole parameter that affected coke dissolution in iron it would be expected that a thicker layer of CA could be formed at the coke interface before it prohibited direct contact of coke and iron, i.e. before it was larger than z_c . It has been reported that the rate of carbon transfer into iron slowed on appearance of CA [2]. It was argued that this was due to densification of the mineral layer at the coke-iron

interface as a result of CA formation, though at the time, wetting/interfacial effects could not be discounted. The contact angle/wetting data presented in paper eliminate the changing wetting characteristics as a cause of slowing down the coke dissolution reaction. As the wetting increases as CA₆→CA₂→CA, CA formation would either have a neutral or positive effect on the rate of carbon transfer/coke dissolution.

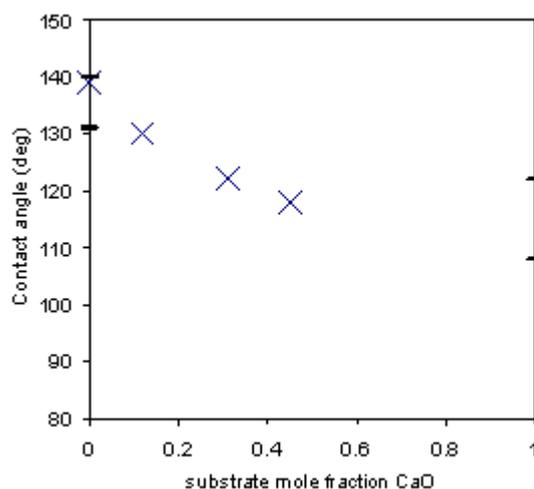


Fig. 3 The influence of substrate on contact angle at 1450°C

3 Conclusions

The contact angle/wetting of a Fe-5%[C] melt on alumina CA₆, CA₂, and CA has been measured and found to decrease with increasing lime content of the substrate. Moreover these results have been used to eliminate changes in interfacial wetting as a result of mineral layer composition changes as a cause for slowing down the rate of coke dissolution in iron.

The effects of temperature on the contact angle were measured over a temperature range of 1450 to 1550°C though no strong correlation was found. At 1550°C there was some evidence of reaction with iron and the alumina substrate. This was considered unusual but has been reported by other researchers and discussed in terms of alumina reduction.

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References:

- [1] Blast Furnace Phenomena and Modelling, eds. Y.E. Omori, London: Elsevier Applied Science, 1987, 58.
- [2]Chapman, M.W., Monaghan, B.J., Nightingale, S.A., Mathieson, J.W., Nightingale, R.J. Formation of a Mineral Layer During Coke Dissolution into Liquid Iron and its Influence on the Kinetics of Coke Dissolution Rate, Metallurgical and Materials Transactions B, 2008, 39B, 418-430.
- [3]Chapman, M.W., Monaghan, B.J., Nightingale, S.A., Mathieson, J.W., Nightingale, R.J. Observations of the Mineral Matter Present at the Coke /Iron Interface During Coke Dissolution, Iron Steel Inst. Jpn. Int., 2007, 47, 973-981.
- [4]Gudenau, H. W. , Mulanza J. P. and Sharma D. G. R. Steel Res., 1990, 61, 97-104.
- [5] Orsten S. and Oeters, F. Process Technology Proceedings, Iron and Steel Society, Washington D.C, Iron and Steel Society, 1986, 143-155.
- [6] Eustathopoulos, N., M.G. Nicholas, and B. Drevet, Wettability at high temperatures. 1st ed. Pergamon Materials series, ed. R.W. Cahn. Oxford: Elsevier Science, 1999.
- [7] ISO, ISO 5017 Dense shaped refractor products - Determination of bulk density, apparent porosity and true porosity. 1998.
- [8] Keene, B.J., Contact angle and work of adhesion between ferrous melts and non-metallic solids, in Slag Atlas 2nd Edition. Duesseldorf: Verlag Sthleisen GmbH, 1995, 513-539.
- [9] Kozakevitch, P. and Urbain G., Mem. Sci. Rev. Metal., 1961, 58, 401- 931.
- [10] Nizhenko, V. and Floka L., Powder Metallurgy and Metallic Ceramics, 1972, 10, 819.
- [11]Keene, B.J., Review of Data for the Surface Tension of Iron and Its Binary Alloys, in Int. Mater. Rev. 1988, 33, 1-37.