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OBSERVATIONS OF THE COKE-METAL INTERFACE ON COKE DISSOLUTION IN SLIQUID IRON

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ABSTRACT

A study into the effects of surface ash formation on the kinetics of coke dissolution in liquid iron has been undertaken. The ash structure has been characterised as the coke dissolution reaction proceeds based on a series of dip tests whereby cokes were immersed in a liquid iron-carbon alloy for a period of time, at a representative ironmaking temperature, then drop quenched, sectioned and polished for optical and electro-optical examination. These experiments were carried out in a laboratory grade argon atmosphere over a temperature range of 1400-1550°C. The coke samples used contained 11.6% ash component. This ash content was refractory in nature with a composition of 54.8% SiO₂, 32.3% Al₂O₃ plus others. On inspection of the coke-iron interface of the samples after each experiment it was found that the presence of an oxide layer at the coke-iron interface was dependant on temperature. At 1550°C no ash layer was found, but in the temperature range 1400-1500°C, an insoluble oxide layer was present at the interface. When present the ash/oxide layer formed a continuous band of oxide at the coke-iron interface. It had a thin ribbon like appearance interspersed with large alumina or calcium aluminate agglomerates. The temperature dependence of the ash formation was explained in terms of a temperature activated time dependant sintering/fusion mechanism and whether the resulting fusion composition contained a significant liquid fraction.

Keywords: Ironmaking, coke dissolution, kinetics, ash, silica reduction

Introduction

It is known that ash formation on coke profoundly affects the rate of coke dissolution in liquid iron^[1,2,3,4,5,6]. The ash is the residue left on the coke granule as the coke is depleted of carbon during coke combustion or coke dissolution. Whilst it has been noted by many workers that the presence of this layer can have a significant affect on the dissolution kinetics^[1,2,3,4,5,6], there has not been a study focussed on characterizing this ash and the growth of this ash on the rate of dissolution. A study into the effects of ash formation on coke on the kinetics of coke dissolution in liquid iron has been undertaken. As part of this study

attempts have been made to characterize the ash structure as the coke dissolution reaction proceeds. It is the results of this characterization study that are presented in this paper.

Experimental

A series of immersion tests were carried out whereby a coke sample was immersed in a liquid iron-carbon alloy for a period of time, then drop quenched, sectioned and polished for optical and electrooptical examination. These experiments were carried out in a laboratory grade argon atmosphere over a temperature range of 1400-1550°C. The temperature range was chosen to replicate what might be expected in the lower

zone-deadman area of a blast furnace. A schematic of the furnace setup and the coke position during the ex-

perimental procedure are given in Figures 1 and 2 respectively.

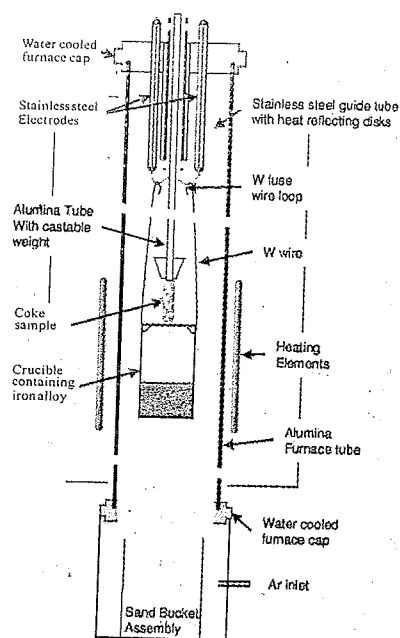


Figure 1 A schematic of the furnace set-up.

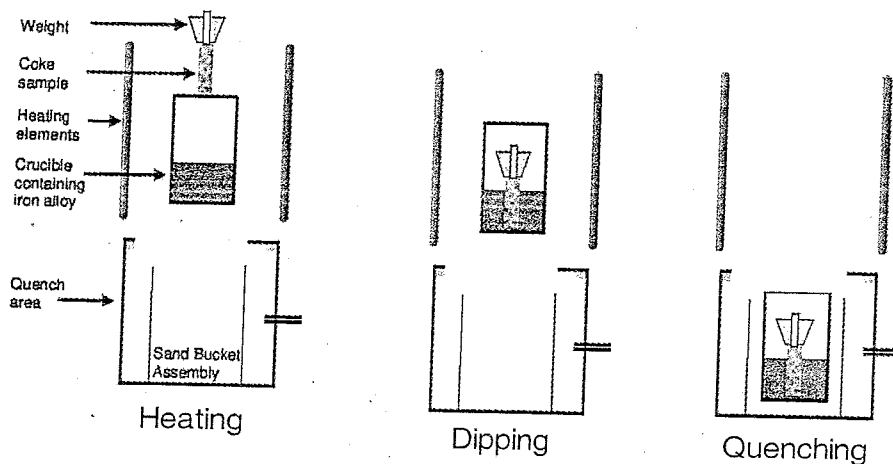


Figure 2 A schematic showing the coke position during the experimental procedure.

The iron carbon alloy was prepared by melting appropriate amounts of electrolytic iron (~ 180g) and spectrographic grade graphite (~ 3.9g) to achieve a 2% carbon-iron alloy prior to dipping the coke materi-

al. Batch analysis of the reagents and resulting iron-carbon alloy composition are given in Table 1. The iron-carbon alloy composition was confirmed using a Leco analyser.

Table 1 Composition of the of reagents and the iron carbon alloy

Mass %	Fe	C	S	Mn	Si	V	O	Other
Electrolytic iron	Bal	0.0078	0.0046	0.08	0.025	0.029	0.3885	<0.01
Iron carbon alloy	Bal	1.98 *	0.004 **	/	/	/	/	/
Mass %	Fe	C	S	Na	Ca	B	Al	Other
Spectrographic grade graphite	2×10^{-4}	Bal	/	5×10^{-4}	4×10^{-4}	1×10^{-4}	1×10^{-4}	$< 5 \times 10^{-4}$

* +/- 0.025% , ** +/- 0.001% , Bal = balance

Coke Sample Preparation and Characterization

The coke samples used were supplied by Blue-Scope Steel and contained approximately 0.4 to 0.45 % S and 11.6% ash component. This ash content was refractory in nature. A detailed ash composition measured by XRFS after ashing at 815°C is given in Table 2.

Table 2 Composition of the of the ash in the coke

Mass %	Ash	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO
	11.6	4.9	54.8	32.3	2.9	1.0
Mass %	P ₂ O ₅	K ₂ O	TiO ₂	Na ₂ O	S	Mn ₃ O ₄
	1.42	0.51	1.4	0.38	0.063	0.05

The supplied coke was cut into rectangular prisms of nominal size 15mm x 15mm x 40-50mm (width x thickness x height) using a diamond saw. These were dried in an oven at approximately 50°C overnight then stored in a desiccator prior to being loaded into the furnace.

The raw unreacted coke was characterised using electron microscopy. The resulting SEM micrograph and elemental maps, measured using EDAX, are given in Figure 3.

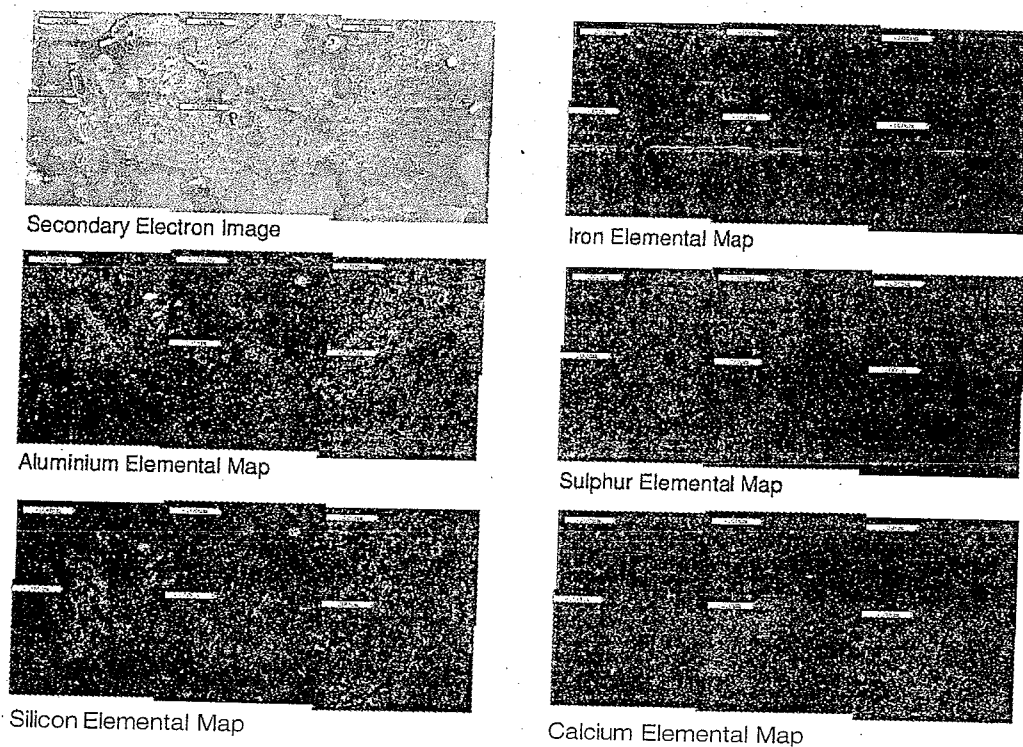


Figure 3 SEM micrograph and elemental maps for the unreacted coke. The scaling bar is 200 μ m.

General observations of the unreacted coke based on Figure 3 are that

- The coke is, as expected, heterogeneous in nature with non carbonaceous matter (ash or oxide phase) dispersed throughout the coke,
- Here is little or no iron in the coke,
- The sulphur present in the coke is below the detection limits of the EDAX technique. The variation in intensity of the sulphur map is a result of sample configuration and not composition.
- The silicon and aluminium are dispersed

throughout the coke. Generally most of the aluminium is coincident with silicon. Silicon is also present independent of any aluminium.

Calcium is found to be dispersed throughout the coke though not necessarily in the same locations as silicon and aluminium.

The peculiarities of the ash/oxide dispersion (aluminium, silicon and calcium oxides) can be explained by reference to the coal formation and coke making processes, see elsewhere^[7] for details.

Results/Discussion

Initial optical inspections of the coke-iron interface of the samples after each experiment showed no evidence of ash on the vertical surfaces of the coke sample. A typical optical micrograph of the coke-iron interface on the vertical surface is given in Figure 4.

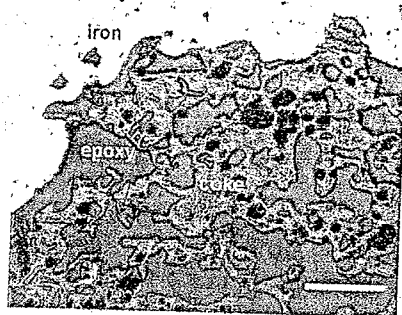


Figure 4 Coke after dissolution in the iron carbon alloy at 1500°C for 20 minutes. The scaling bar is 380 μm .

To assess whether the apparent lack of an oxide/ash layer on the surface was a consequence of the relatively low resolution used in the optical microscopy, a series of higher resolution images and EDAX analysis

was carried out using the SEM. This analysis was carried out over large portions of the coke-iron interface. At high magnification an ash layer was observed and a typical coke-metal interface for 1400°C and 1450°C is shown in Figure 5.

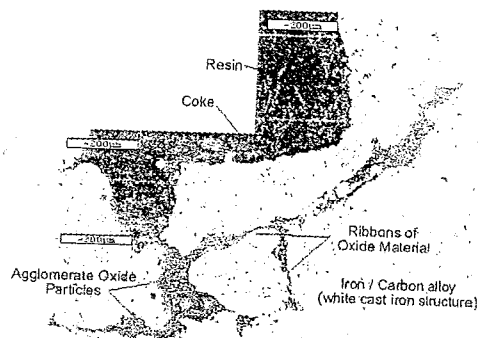


Figure 5 QBSD Micrograph of the coke-iron interface at 1450°C after 20 minutes of dipping showing typical features of oxide particle agglomeration and interconnecting ribbons of oxide material. The scaling bar is 200 μm .

Details of the structure and composition of the agglomerated particles observed at 1400°C and 1450°C are given in Figures 6 and 7, while Figure 8 represents a typical section of the 1500°C coke-metal interface.



Figure 6 Micrograph and map of the oxide agglomeration at the coke-iron interface at 1400°C after 20 minutes of dipping. The scaling bars on the micrographs and maps are 30 and 50 μm respectively.



Figure 7 Micrograph and map of the oxide agglomeration at the coke-iron interface at 1450°C after 20 minutes of dipping. The scaling bars on the micrographs and maps are 20 and 50 μm respectively.

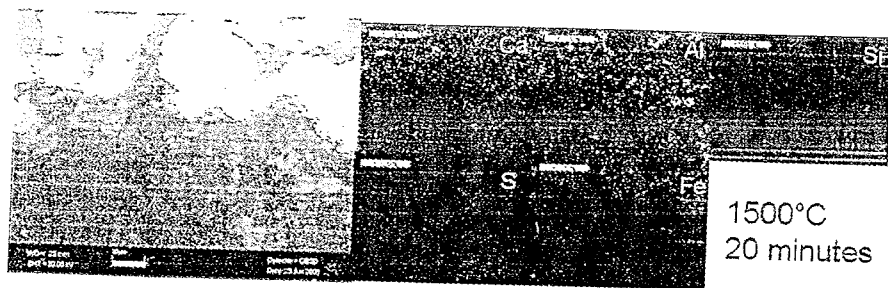


Figure 8 Micrograph and map of the oxide agglomeration at the coke-iron interface at 1500°C after 20 minutes of dipping. The scaling bars on the micrographs and maps are 20 and 50 μm respectively.

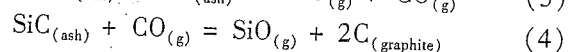
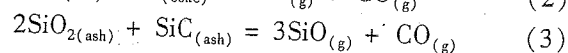
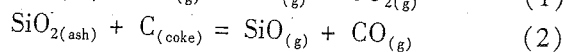
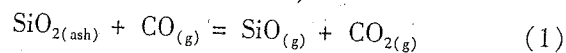
A summary of key observations of the experiments and the SEM analysis are given in Table 3.

Table 3 Observations and experimental summaries of the 20 minute dipping experiments.

Experimental temperature	Observation
All	Often there was a gap found between the iron and the coke at the coke-metal interface. When an ash or oxide layer was found it tended to be on the metal side of the gap. The profile of this ash/oxide layer is usually mirrored by the coke profile. It is believed that this gap formed on quenching.
	There was little or no silica at the coke-metal interface nor in any of the oxide agglomerations or ribbons of oxide material.
	The coke both close and distant from the coke-metal interface was depleted in silicon.
	Although initially present in the coke and found by LE-CO analysis in the iron after quenching, there was no sulphur or calcium sulphides observed at the coke-metal interface at any of the temperatures studied.
1400°C and 1450°C	There was a continuous band of alumina along the iron side of the gap at the coke iron interface. It had a thin ribbon like appearance interspersed with large alumina or calcium aluminate pieces (100 μm), see Figure 5. The majority of these larger pieces were alumina. Figure 6 shows a micrograph of a predominately alumina agglomeration and Figure 7 a micrograph of a calcium aluminate agglomeration.
	The large alumina pieces were found to be agglomerates of small angular alumina particles.
	The coke side of the gap at the coke-iron interface has very little oxide associated with it.
1500°C	The ash/oxide layer is typically attached to the coke at the coke-iron interface.
	The large agglomerated particles were less angular than at lower temperature experiments. This is thought to be evidence of melting or softening.
1550°C	There was little evidence of an oxide/ash layer at the coke-iron interface.
	A slag had formed on the surface of the liquid iron. This was not observed in the lower temperature experiments.

Loss of Silicon

The loss of silicon from within the coke and the fact that silicon was not observed in the ash/oxide layer is not completely unexpected. There are a number of possible coke reactions that result in the formation of $\text{SiO}(\text{g})$ (equations 1 to 4) [8]

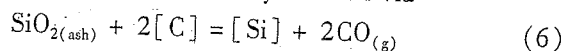


Once this gas is formed, silicon may leave the coke in the gas phase or react with the liquid iron via

$$\text{SiO}_{(\text{g})} + [\text{C}] = [\text{Si}] + \text{CO}_{(\text{g})} \quad (5)$$

Generally equation (2) would be considered the most dominant reaction for $\text{SiO}(\text{g})$ generation in a coke sample.

Any silica that remains in the coke as the ash/oxide layer is exposed to the carbon containing liquid iron may also be reduced by the iron via



Loss of silicon from the coke via the gas phase or reaction with the liquid iron has been confirmed by silicon analysis of the iron samples and fume collected on the furnace cap.

Layer formation

The purpose of this study was to characterise the oxide layer that forms on the surface of coke as the coke (carbon) dissolution takes place. This was being carried out with a view to improving our understanding and modelling capability of the coke dissolution process. Not surprisingly, it has been found that for the coke studied, the form of the oxide at the coke-iron interface was found to be dependent on temperature. At

1550°C no oxide layer was found at the coke-iron interface though a slag formed on the surface of the melt. At 1500°C and at lower temperatures an ash/oxide layer was found at the interface. The larger agglomerates associated with the ash/oxide layer were more angular at lower temperatures.

A convenient answer as to why there is no oxide layer at the coke-iron interface at 1550°C is that the ash/oxide would have been liquid when exposed to the liquid iron during the dissolution process and once exposed, floated to the melt surface to form a slag. Thermodynamic calculations using MTDATA^[9] on a reduced ash composition containing only Al₂O₃-SiO₂-CaO-MgO-Fe₂O₃-Na₂O (approximately 96% of listed ash components in Table 2) showed a 10% increase in the liquid phase present when the temperature was increased from 1400°C to 1550°C. At 1400°C the ash had a calculated liquid fraction of ~70% and at 1550°C ~80%. The thermodynamic calculations make it difficult to conclude that a simple argument based on the liquidus temperature or amount of liquid present is responsible for there being no ash at the coke-iron interface. It should be noted that the calculated liquid fractions are based on no loss of silicon from the coke. Given our results and previous discussion on silicon losses, this is not the case and these % liquid values would be an overestimate.

Due to the nature of the coal and coke formation processes, the mineral matter within the coke consists of numerous individual assemblages from each of the coals in the blend. The assemblages are diverse and complex, containing both oxide compounds such as alumina-silicates and discrete oxides such as quartz and other minor oxides^[7,10,11]. There is evidence of this in our raw coke maps in Figure 3, where it can be seen that the silicon, aluminium and calcium are not all coincident. That being the case it, the fusion of the mineral matter is also complex and it may take a significant amount of time for the components to fuse and to approach the equilibrium liquid levels calculated using MTDATA. This fusion process would involve sintering and be complicated by the need for mass transport of oxide components that are not coincident. Such a process would be temperature activated and be expected to be faster at higher temperatures^[12]. It is likely

that it is a combination of a temperature activated fusion process and its effects on the amount of liquid present in the ash/oxide that are critical in determining whether the ash remains on the coke or floats to the surface. A further complication in understanding the effects of this fusion process would be transient effects of loss of silicon from the coke. As mentioned previously this loss of silicon, for the composition of coke studied, would lower the amount of liquid present.

The proposed fusion process is consistent with the lower temperature (1500°C to 1400°C) results where an oxide layer formed at the interface. The large agglomerates shown in Figures 6-8 are less angular at the higher temperature (1500°C). It is likely that the more rounded small particulates that make up the larger agglomerates at 1500°C are being softened or were partially molten at some stage due composition changes resulting from a temperature activated fusion (sintering) process.

Consequences for Coke Dissolution in Iron

The changes observed in the ash-oxide layer at the coke iron interface at different temperatures may have a significant effect on the coke dissolution kinetics. At 1550°C there is no ash-oxide barrier to inhibit carbon dissolution in iron, therefore coke dissolution will be less hindered. Also when an ash layer is present at the higher temperature (1500°C) it is likely that the effective porosity will be lower (layer density higher) due to sintering than that of the 1400 and 1450°C experiments. Under such conditions it would be expected that the ash/oxide layer would provide more resistance to coke dissolution than at 1400°C and 1450°C experiments. For all other things being equal, this would result in a slower rate of dissolution of coke in liquid iron. These indications will be studied quantitatively in subsequent work.

Conclusions

A series of experiments have been carried out in an attempt to characterize the ash/oxide layer formed on a coke particle as it dissolves in liquid iron. It was found that

1. The presence of an ash layer at the coke-iron interface was dependant on temperature. At 1550°C no ash layer was found but in the temperature range

- 1400-1500°C a layer was present at the interface.
- ii. When present the ash/oxide layer formed a continuous band of oxide at the coke-iron interface. It had a thin ribbon like appearance interspersed with large alumina or calcium aluminate agglomerates.
 - iii. The large alumina and calcium aluminates agglomerates were made up of smaller particulates.
 - iv. The form of the ash layer seemed to be dependant on temperature. The large alumina or calcium aluminate agglomerates were more angular at lower temperatures suggesting a softening or melting of the smaller particulates at higher temperatures.
 - v. The temperature dependence of the ash formation was explained in terms of a temperature activated time dependant sintering/fusion mechanism and whether the resulting fusion composition contained a significant liquid fraction.
 - vi. There was loss of silicon from the ash/oxide in the coke. This was attributed to SiO gas generation and silica reduction by the liquid iron.

Acknowledgements

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