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SULPHIDE FORMATION DURING COKE DISSOLUTION IN LIQUID IRON

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Abstract

An experimental study on mineral layer formation at the coke-iron boundary during coke dissolution has been carried out. In previous articles by the authors the focus was on morphology of layer development and its effects on the kinetics of coke dissolution. In this article the formation of calcium sulphide at the coke-iron boundary is discussed. The compositions and temperatures used in the experimental set up were chosen to represent coke-iron mass ratios of the lower zone of an iron blast furnace.

SEM images and EDS analysis of the coke-iron interface revealed a mineral layer at the interface. This layer was found to be primarily calcium aluminate based that over time (0-120 minutes) became progressively enriched with calcium. The ratios of calcium and aluminium found in the mineral layer indicate that the layer is composed of alumina, CA6, CA2 and CA.

A sulphide layer was also observed in these experiments after the establishment of a calcium rich calcium aluminate (CA2 and in particular CA). Thermodynamic analysis of the calcium aluminates formed during coke dissolution was carried out to establish the stability of <CaS> in the experimental set up. From the results presented and the coke composition studied it can be concluded that formation of calcium rich calcium aluminates are a necessary precursor to <CaS> formation.

Introduction

Coke is a critical reagent in the production of blast furnace iron. It is the furnace fuel, enabling the furnace to achieve the high temperatures required for economic iron production, it dictates the gas and liquid flow distribution within the furnace, and is the source of carbon in the liquid iron product [1]. There are a number of reaction regimes coke experiences in a blast furnace that need to be delineated if the coke's reaction behaviour in the furnace is to be understood. In this study coke liquid iron reactions occurring in the hearth below the slag layer are examined. Of particular interest is the nature of the mineral layer formed at the coke-liquid iron interface as coke dissolution proceeds. Liquid iron entering this region contains more than 2 mass% C, and picks up its final carbon while percolating through the packed coke bed in the deadman and hearth of the blast furnace [1]. Metallurgical coke typically contains 8-12% by mass inorganic mineral matter [2]. As coke is dissolved in the liquid iron, there is potential for the insoluble components of this inorganic mineral matter to form a layer at the surface of the coke inhibiting carbon dissolution [3,4,5,6,7,8,9,10,11,12].

There are little data on the form, composition and morphology of the layer that forms during coke dissolution in liquid iron. Recent studies by the current authors [3,4,5] have related direct measurements and observations of the composition and morphology of the mineral layer formed at the coke-liquid iron interface to the rate of coke dissolution. The mineral layer formed was primarily a calcium aluminate that progressively became enriched in calcium as the dissolution reaction proceeded. The calcium enrichment led to a change in morphology of the mineral layer that in turn slowed the rate of coke dissolution. This work [4,5] clearly demonstrated the link between coke dissolution kinetics and the morphology of the mineral layer formed at the coke-iron interface. Phase morphology is in part a function of composition. It is therefore expected that any mineral morphological effects of the layer at the coke-iron interface on the rate of coke dissolution will be a function of the coke mineral composition. Details of sulphide formation were not discussed in these articles but are elaborated as the main subject of this paper.

Other data that have specific details on what type of layer forms on the coke as dissolution reaction proceeds comes from an excellent study by Gudenau et al [6] who presents data of ash (mineral matter) found on the surface of cokes dipped in liquid iron and from sessile drop studies by Sahajwalla's research group [9,10,11,12].

Gudenau et al [6] investigated industrial cokes and speciality cokes that had their mineral component modified with oxides (SiO_2 , CaO , MgO , Al_2O_3 and Fe_3O_4). After dipping (and rotating) in liquid iron the surface of the coke was analysed. Gudenau et al [6] found ash (mineral matter) on the coke surface and argued that this ash layer was responsible for observed changes in the coke dissolution rates. The addition of refractory oxides, CaO , MgO , Al_2O_3 to the coke decreased the dissolution rate, whereas the addition of iron oxide enhanced the dissolution rate.

In the liquid iron sessile drop studies [9,10,11,12], where a drop of liquid iron is reacted with a carbonaceous substrate, it was found that an ash (mineral) layer formed at the iron-carbonaceous material interface. General observations of the droplet surface in these studies indicate that although silica was contained in the carbonaceous material, there was none present in the ash at the interface. The ash (mineral) layer at the interface was initially Al_2O_3 , however as the reaction time increased, the proportion of CaO increased, after which the Al_2O_3 was observed to disappear from the droplet-coke interface and was replaced by an iron

calcium sulphide. Although these studies are instructive in identifying potential features of a mineral matter layer at the metal coke interface, the coke-metal mass ratios used are not typical of those found in the hearth of a blast furnace. In this area, below the slag line the coke is immersed in the iron. In a sessile drop experiment a small finite amount of iron is sitting on a substrate of coke or carbon. Under such conditions it would be expected that the coke-metal ratio of the blast furnace would be much lower, with the potential for silicon and sulphur levels of the metal as a result of coke dissolution to also be much lower. This would have a significant impact on any mineral layer formed at the interface [3].

In this paper sulphur and sulphide formation during coke dissolution in liquid iron are presented and discussed.

Experimental

A series of coke (carbon) dissolution experiments were performed whereby 10g of crushed coke was added directly to the top surface of 164g of liquid iron 2 mass% carbon alloy. The melt plus coke were held at temperature for a period of time ranging from 2 to 120 minutes. At the end of this time, the crucible containing the melt and coke was quenched by lowering it into a water cooled stainless steel quenching chamber fitted to the bottom of the furnace. The experiment including the quenching was carried out in a dry flowing argon atmosphere. After quenching the samples were sectioned and prepared for electro-optical examination. Experiments were conducted over the temperature range of 1450-1550°C. The temperatures were chosen to replicate what might be expected in the lower zone deadman area of a blast furnace. A schematic showing the furnace and sample configuration used is given in Figure 1.

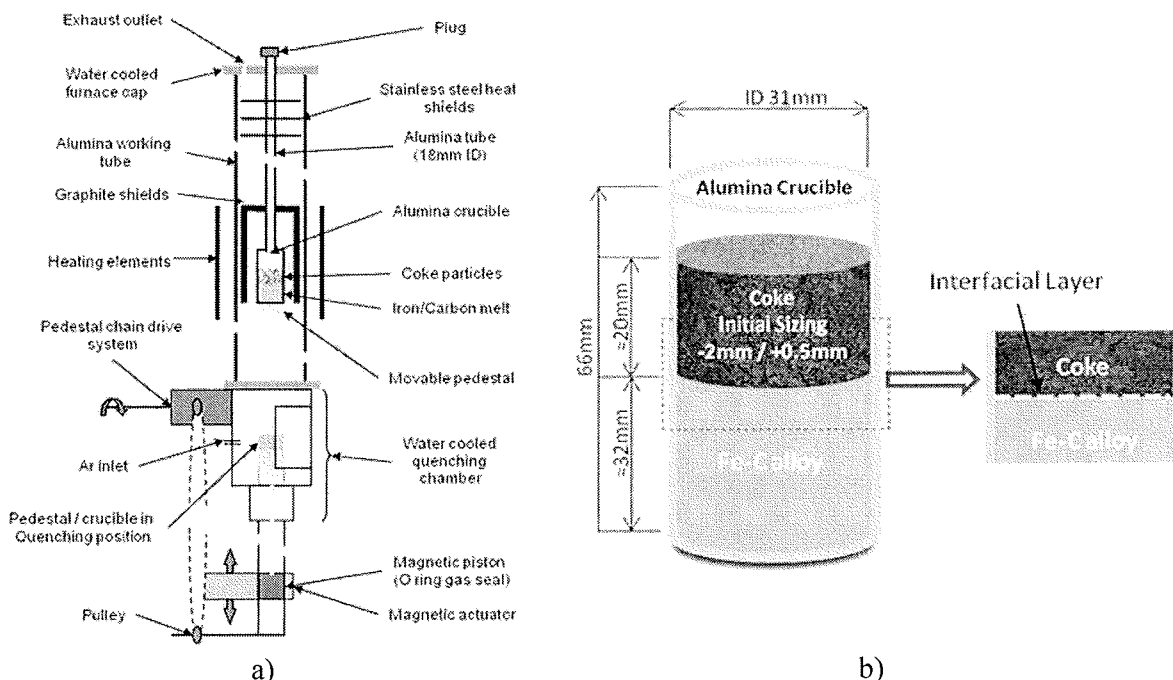


Figure 1. Schematic showing a) the furnace set-up and b) melt configuration used in the quenching experiments

Raw Materials

The iron carbon alloy was prepared by melting appropriate amounts of electrolytic iron and coarsely crushed spectrographic grade graphite rod to achieve a 2% carbon-iron alloy prior to

the addition of the coke. The initial melt composition is given in Table 1. Carbon and sulphur analysis of the iron was performed using a LECO CS-444 analyser. Analysis of other elements in the iron was performed by atomic emission spectroscopy, at the metallurgical laboratories of BlueScope Steel on disks of iron machined from the middle of the quenched iron sample.

Table 1. Initial melt composition (mass%)

[C]	[S]	[Si]	[Ti]	[Mn]
2.03	0.005	0.04	0.029	0.03

The coke samples used were provided by BlueScope Steel and contained approximately 0.4 – 0.45 mass% sulphur and 11.6 mass% inorganic material (ash). A detailed oxide composition measured by XRF after ashing at 815°C is given in Table 2.

Table 2. Mass % compositions of the of the oxide components in the coke

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

Sample Preparation

The quenched crucible containing the iron alloy and coke was impregnated with liquid resin under vacuum to preserve the coke-metal interface during sectioning. Lead shot was added to the top of the coke inside the crucible, before the resin impregnation to minimise coke movement during the vacuum impregnation procedure. The bottom section of the crucible was removed and iron samples for analysis were machined from the iron block. A vertical cut was made across the centre of the sample exposing the coke-metal interface. The interface was mounted and prepared for SEM analysis. Compositional analysis of the coke and mineral layer in the quenched sample were made using an SEM EDS system.

Results

The carbon dissolution kinetics and mineral layer formation have been discussed in detail elsewhere [3,4,5,13], including Scanmet III [13]. What follows is a brief summary of the layer formation presented in these papers and new data relating to sulphur transfer during coke dissolution and sulphide formation not presented previously.

As the coke dissolution reaction proceeded a mineral layer was formed at the coke-liquid iron interface. The mineral layer was found to be principally composed of calcium aluminates, see Figures 2 and b for details. The ratios of calcium and aluminium found in the mineral layer indicate that the mineral layer is composed of alumina, CA6, CA2 and CA.

As the coke dissolution reaction continues the predominant structure changes from a loose agglomeration of primarily alumina particles to an open porous network of acicular needles. These needles are still predominately Al₂O₃, but also contain an increased proportion of calcium in the form of CA6. Further dissolution, increases the calcium enrichment of the mineral layer. This layer retains a relatively open structure however the fine needles are replaced by coarser structure of CA6 and CA2. As the dissolution reaction time continues, further calcium enrichment of the mineral layer is observed resulting in a CA+CA2 structure. As the CA is formed the mineral layer changes from an open structure to a dense layer.

This change from an open to dense layer is coincident with a significant slowing in the rate of coke dissolution in iron. The authors [5, 13] argue that the formation of this dense layer inhibits carbon transfer to the metal by lessening the contact area between the coke and iron. The change of layer structure with time is given in Figures 2 a and b. It should be noted that as coke dissolves in iron, mineral phases present with in the coke are being exposed to, and interact with, the mineral layer at the coke-iron interface. This exposure results in a phase and composition gradient in the layer at all experimental times. Therefore although for example, a predominant layer of CA+CA2 is discussed, it is expected that there are small quantities of other minerals such as Al₂O₃ at the mineral layer-coke interface.

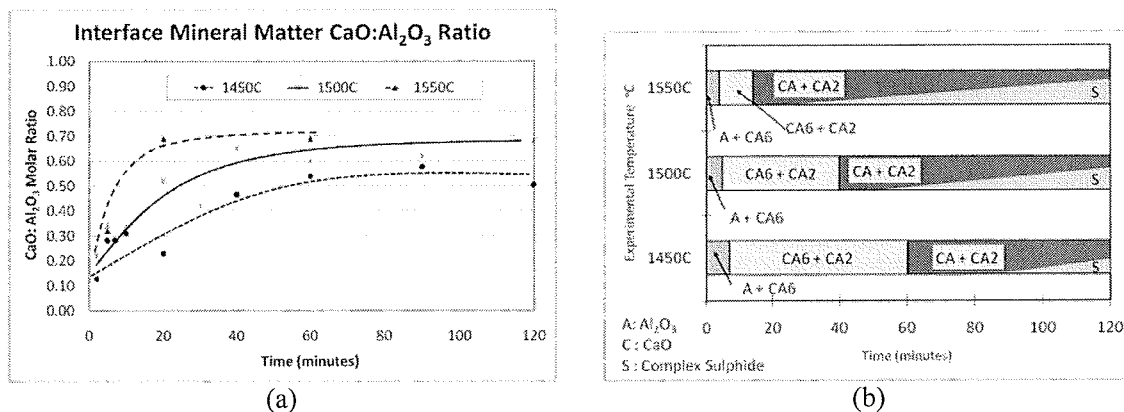


Figure 2 a) Molar CaO-Al₂O₃ ratio verses experimental time. b) Predominant mineral matter phase(s) at the coke – metal interface verses experimental time.

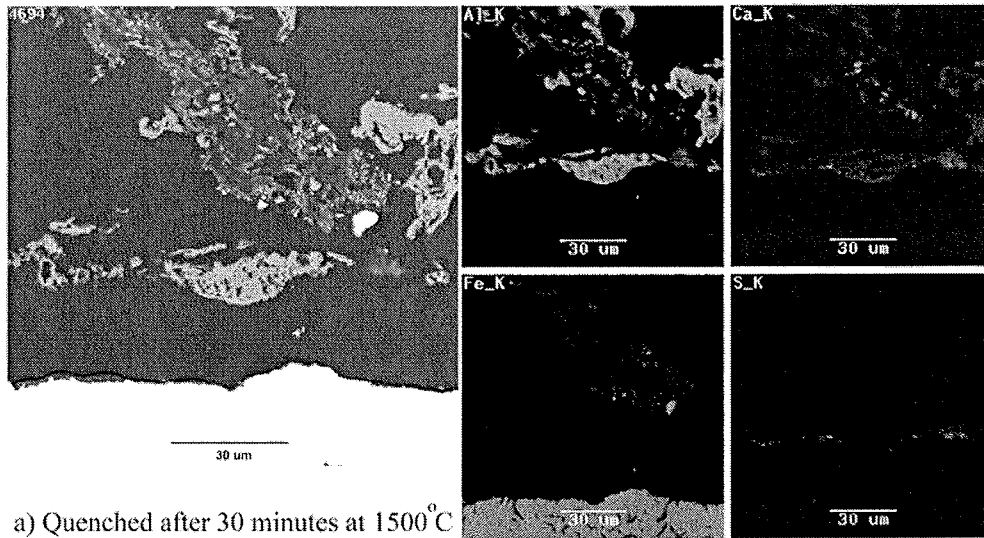
Though the predominant phases of the mineral layer were calcium aluminate based there was also evidence of sulphide formation. Typical SEM-EDS maps obtained of the interface are given in Figures 3 a to c. In Table 3 details of sulphide formation and when the sulphide formed are noted. These details are based on SEM-EDS mapping of the coke-iron interface.

Table 3. Details of sulphide formation during coke dissolution experiments

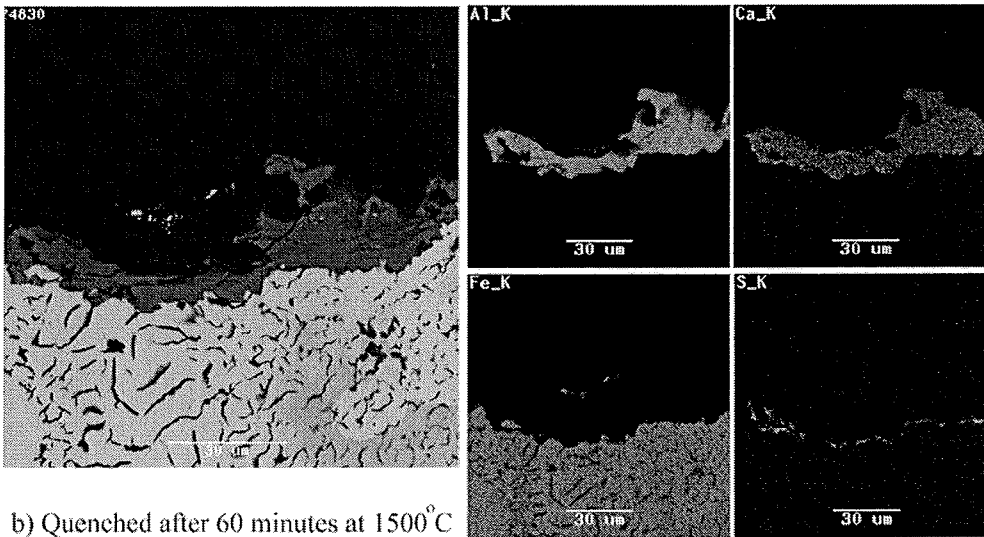
Temperature	Time in minutes				
	2	5	7	10	20
1450°C	none	none	none	none	none
1500°C	none	none	/	slight	slight
1550°C	/	none	/	/	fine layer
Temperature	Time in minutes				
	30	40	60	90	120
1450°C	/	none	none	slight	fine layer
1500°C	slight	fine layer	fine layer	fine layer	thick layer
1550°C	/	/	thick layer	/	thick layer

In Table 3 “/”, indicates no sample, “none” indicates no sulphide phase found, “slight” indicates small discrete particles found but no continuous sulphide layer observed (see Figure 3a for an example), “fine layer” indicates a fine continuous layer at the iron side of the mineral layer interface (see Figure 3b for an example) and “thick layer” indicates a thicker continuous sulphide layer extending into the mineral layer from the iron side of the interface (see Figure 3c for an example).

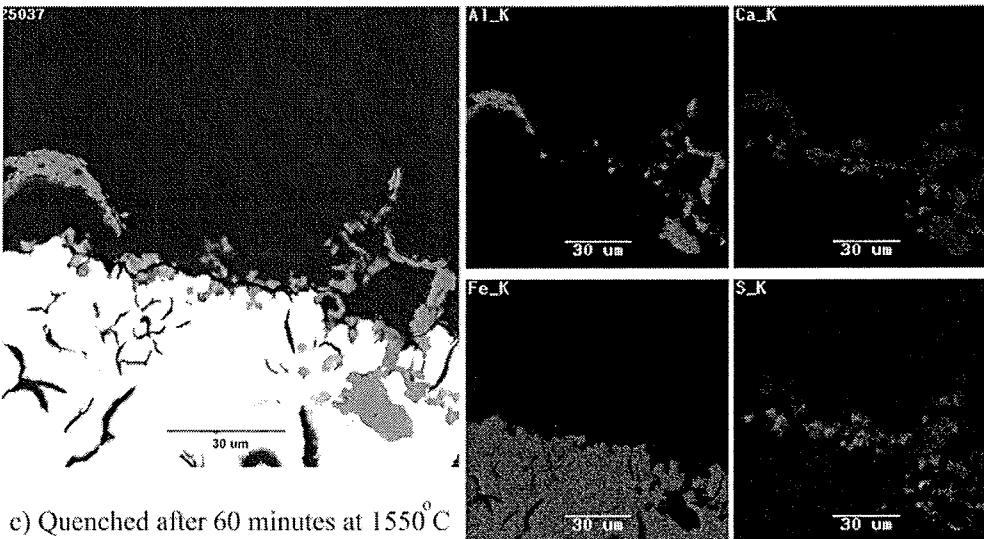
Sulphur pickup in the metal is given in Figure 4 and average melt compositions are given in Table 4. The lines shown on Figure 4 have been drawn to be representative of the [S] transients at different temperatures.



a) Quenched after 30 minutes at 1500°C



b) Quenched after 60 minutes at 1500°C



c) Quenched after 60 minutes at 1550°C

Figure 3. SEM Backscattered electron images and elemental EDS maps of mineral layer quenched after a) 30 minutes at 1500°C b) 60 minutes at 1500°C c) 60 minutes at 1550°C. The scaling bar is 30 μm.

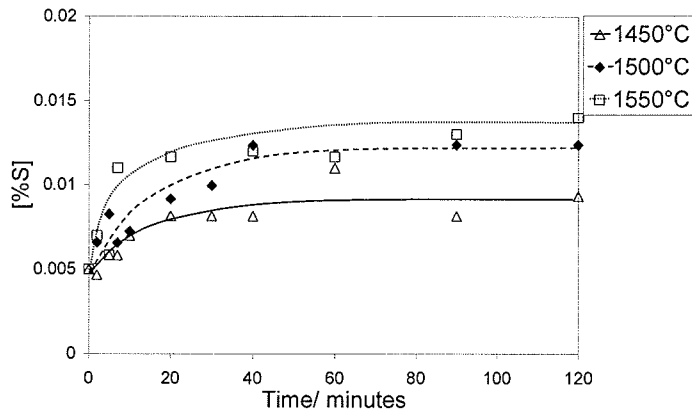


Figure 4. [%S] with time for temperatures 1450, 1500 and 1550°C

Table 4. Average melt compositions relating to plateaus in the [%C] (see references [4,5]) and [%S] transients.

	[C]	[S]	[Si]	[Ti]	[Mn]
1450°C	3.05	0.008	0.063	0.033	0.03
1500°C	3.6	0.012	0.098	0.051	0.03
1550°C	4.67	0.013	0.13	0.05	0.03

From Figure 4 it can be seen that the rate and amount of sulphur pick up in the melt increases with increasing temperature.

Discussion

Due to limitations of space detailed discussion of the kinetics of sulphur transfers of these results has not been attempted. What is discussed is the stability of <CaS> in the experimental setup. It is assumed that the sulphide observed in Figures 3 a to c is <CaS>. The basis for this assumption is that the sulphur is always associated with calcium when mapped and not Al or Fe. Since coke contains sulphide minerals [14] there is the possibility of <CaS> (or other sulphide minerals) arriving at the coke-iron interface as part of the coke mineral matter exposed to the mineral layer as the coke dissolution reaction proceeds. This is unlikely to be responsible for the <CaS> observed in this study. The sulphide bearing mineral matter is primarily observed on the metal side of the mineral layer. If the sulphide that was being observed in the mineral layer was a result of build-up of sulphur bearing minerals released from the coke as carbon is dissolved in the iron it may be expected that the sulphur layer would appear throughout the mineral layer.

Employing relevant thermodynamic data on a_{CaO} to represent the changes in the mineral layer as a result of calcium enrichment, <CaS> formation can be represented by Equation 1.



An equilibrium Gibbs free energy equation for Equation 1 is given in Equation 2.

$$\Delta G^\circ = 371510 - 199.36T \quad \text{J.mol}^{-1} \quad (2)$$

Equation 2 has been obtained using the equilibrium Gibbs free energy relations in Table 5. Evaluating the ΔG° (Equation 2) over the experimental temperature range gives positive

values indicating the formation of <CaS> in Equation 2 is not favoured. Therefore, under standard equilibrium conditions no significant amount of <CaS> would be expected to form at the mineral layer from this reaction. The experiments are not at equilibrium though. Therefore simple calculations based on equation (2) are likely to be misleading. Gibbs free energy calculations based on the prevailing condition at the coke iron interface using Equation 3 may be more relevant.

Table 5. Tabulated thermodynamic data [15]

Reaction	Gibbs free energy in J.mol ⁻¹
$\frac{1}{2}(\text{O}_2) = [\text{O}]_{1 \text{ wt}\%}$	$\Delta G^\circ = -115750 - 4.63T$
$\frac{1}{2}(\text{S}_2) = [\text{S}]_{1 \text{ wt}\%}$	$\Delta G^\circ = -135060 + 23.43T$
$\{\text{Ca}\} + \frac{1}{2}(\text{O}_2) = \langle \text{CaO} \rangle$	$\Delta G^\circ = -900300 + 275.1T$
$\{\text{Ca}\} + \frac{1}{2}(\text{S}_2) = \langle \text{CaS} \rangle$	$\Delta G^\circ = -548100 + 103.8T$
$\langle \text{C} \rangle_{\text{graphite}} + \frac{1}{2}(\text{O}_2) = (\text{CO})$	$\Delta G^\circ = -114400 - 85.8T$

$$\Delta G = \Delta G^\circ (\text{Equation 2}) + RT \ln \left(\frac{a_{\langle \text{CaS} \rangle} \cdot h_{[\text{O}]}}{a_{\langle \text{CaO} \rangle} \cdot h_{[\text{S}]}} \right) \quad (3)$$

The ΔG in Equation 3 was evaluated using initial [S] given in Table 1 and plateau [S] given in Table 4 for all experimental temperatures and the results are given in Table 6. Negative ΔG values indicate that the sulphide formation in Equation 2 is favoured, positive values indicate sulphide formation is not favoured. It should be noted that ΔG 's calculated from Equation 3 are not equilibrium values but represent a transient free energy condition.

Table 6. Calculations of ΔG under experimental conditions in kJ. mol⁻¹.

T/°C	Initial melt [S]			Plateau melt [S]		
	A+CA6	CA6+CA2	CA+CA2	A+CA6	CA6+CA2	CA+CA2
1450	49.1	30.5	2.7	42.4	23.8	-4.0
1500	39.1	20.2	-8.6	26.2	7.3	-21.5
1550	29.0	9.8	-20.0	14.5	-4.6	-34.5

The calculations presented in Table 6 were made assuming that <CaS> was pure and therefore had an activity of 1 and that [S] showed ideal Henrian behaviour. The $h_{[\text{O}]}$ was calculated from the Gibbs free energy of reaction for Equation 4 assuming a $p_{\text{CO}}=1$ atm and pure graphite, that is a $a_{\langle \text{C} \rangle_{\text{graphite}}}=1$. The ΔG° for Equation 4 was obtained from the tabulated data in Table 5. ΔG° in Equation 3 is obtained from the Equation 2.



Changes in $a_{\langle \text{CaO} \rangle}$ in the mineral layer due to calcium enrichment (shown in Figures 2 a and b) for the different phase regions were calculated using MTDATA [16] thermodynamic software and are given in Figure 5.

From Table 6 it can be seen that the sulphide formation is only favoured at 1500 and 1550°C when CA+CA2 are present in the layer. At plateau compositions in the melt sulphide formation is favoured at 1550°C when CA6+CA2 is present and at all temperatures when CA+CA2 is present. The ΔG values in Table 6 are reasonably consistent with what is observed in the SEM-EDS maps obtained in this study, examples of which are given in Figures 3 a to c, and Table 3. The only significant deviation from the calculated results reported in Table 6 and that in Table 3 relate to the early times (10 to 30 minutes) at 1500°C.

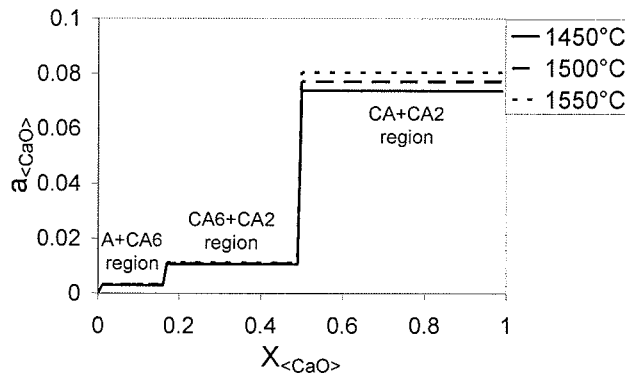


Figure 5. The a_{CaO} in calcium aluminates as calculated by MTDATA [16].

In 1500°C experiment at these times small discrete particles of sulphide were found but no continuous sulphide layer observed. This discrepancy is most probably a result of some early CA phase formation not detected in the SEM-EDS analysis. From the sulphide formation results obtained in our investigation it can be concluded that formation calcium rich calcium aluminates (CA2 and in particular CA) are a necessary precursor to $\langle \text{CaS} \rangle$ formation.

Conclusions

In an experimental study on mineral layer formation at the coke-iron boundary during coke dissolution it was found the formation of a calcium rich calcium aluminate (CA2 and in particular CA) preceded any $\langle \text{CaS} \rangle$ formation. Thermodynamic analysis of the experimental results confirmed that the enriched calcium aluminate formation was a necessary requirement to stabilise $\langle \text{CaS} \rangle$ for the coke composition studied.

Acknowledgments

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List of symbols used in text

Symbol	Definition	Symbol	Definition
$\langle \rangle$, $\{ \}$ and $()$	Solid, liquid and gas phase	CA _x	CaO.xAl ₂ O ₃
[]	Solution in metal phase	X _i	Mole fraction of i
ΔG° , ΔG	Gibbs free energy	a _i	Raoultian activity of i
[] _{1 wt%}	1 weight % reference state	h _i	Henrian activity of i
R	Gas constant 8.314 J.mol ⁻¹ K ⁻¹	T	Temperature in K

References

- [1] Blast Furnace Phenomena and Modelling, ed. Y.E. Omori, (London, UK: Elsevier Applied Science, 1987), 58.
- [2] P. Loison, P. Foch, A. Boyer: Coke Quality and Production, (London, UK, Butterworths 1989), 159.
- [3] M.W. Chapman, B.J. Monaghan, S.A. Nightingale, J.G. Mathieson, R.J. Nightingale: "Observations of the Mineral Matter Present at the Coke /Iron Interface During Coke Dissolution", ISIJ International, 47, (2007), 973-981.

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- [4] M.W. Chapman, B.J. Monaghan, S.A. Nightingale, J.G. Mathieson, R.J. Nightingale: "Observations Of The Coke-Metal Interface On Coke Dissolution In Liquid Iron", Australia-China-Japan Symposium on Iron and Steel Making, Shenyang, China, 2006, 90-96.
- [5] M.W. Chapman, B.J. Monaghan, S.A. Nightingale, J.G. Mathieson, R.J. Nightingale: "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, submitted in September 2007.
- [6] H.W. Gudenau, J.P. Mulanza, D.G.R. Sharma: "Carburization of Hot Metal by Industrial and Special Cokes", Steel Research 61(1990), 97.
- [7] S. Orsten , F. Oeters: Process Technology Proceedings, Iron and Steel Society, Washington, D.C, USA, 1986, 143.
- [8] M.B. Mourao, G.G.K. Murthy, J.F. Elliott: "Experimental Investigations of Dissolution Rates of Carbonaceous Materials in Liquid Iron--Carbon Melts", Metallurgical Transactions B, 24B, (1993), 629.
- [9] R. Khanna, F. McCarthy, H. Sun, N. Simento, V. Sahajwalla: "Dissolution of Carbon from Coal-Chars into Liquid Iron at 1550°C" Metallurgical and Materials Transactions B, 36B, (2005), 719.
- [10] F. McCarthy, R. Khanna, V. Sahajwalla, N. Simento: "Interfacial Phenomena Occurring During Iron/Char Interactions in a Blast Furnace" ISIJ International, 45, (2005), 1261.
- [11] F. McCarthy, V. Sahajwalla, J. Hart, N. Saha-Chaudhury: "Influence of Ash on Interfacial Reactions between Coke and Liquid Iron" Metallurgical and Materials Transactions B, 34B, (2003), 573.
- [12] C. Wu , R. Wible, V. Sahajwalla: "Influence of Ash on Mass Transfer and Interfacial Reaction between Natural Graphite and Liquid Iron" Metallurgical and Materials Transactions, 31B, (2000), 1099.
- [13] M.W. Chapman, B.J. Monaghan, S.A. Nightingale, J.G. Mathieson, R.J. Nightingale:" Coke Dissolution In Liquid Iron - The Effect Of Coke Mineral Matter", Scanmet III, Luleå, Sweden, June 2008.
- [14] S. Gupta, M. Dubikova, D. French, and V. Sahajwalla: "Characterization of the Origin and Distribution of the Minerals and Phases in Metallurgical Cokes", Energy & Fuels 21(2007), 303-313.
- [15] E.T. Turkdogan: fundamentals of Steelmaking (London, UK, The Institute of Materials, 1996), 10 and 95.
- [16] R.H. Davies, A.T. Dinsdale, J.A. Gisby, S.M. Hodson, R.G.J. Ball: Conference On Applications Thermodynamics on the Synthesis and Processing of Materials, ASM/TMS, Rosemont, IL, USA, (1994), 371.