Insoluble oxide product formation and its effect on coke dissolution in liquid iron

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NOTE

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“Knowledge is knowing that you are on a one way street, wisdom is looking both ways anyway”

Unknown

7. Conclusion

A detailed investigation was conducted examining the influence of coke mineral matter on coke (carbon) dissolution into liquid iron. The focus of this project was the mineral matter layer that forms at the coke/iron interface and how the presence of this layer affects the kinetics of carbon dissolution from the coke into the liquid iron. A range of experimental techniques were used to identify and characterise the mineral layer that formed at the coke/iron interface, and to assess the layers influence on the carbon dissolution kinetics. The coke dissolution experiments were complemented by a series of dissolution experiments were a coke analogue was used as the carburising agent. The coke analogues had been designed to be coke like in the key aspects of porosity, bulk density and contained multiple forms of carbon. However, unlike coke, the coke analogues had consistent and predictable structure and composition. The composition of the mineral matter components in the coke analogue could also be controlled.

The dissolution studies were further complemented by sessile drop measurements of the wetting behaviour of iron on the mineral phases that were identified in the mineral layer present at the coke/iron interface, thermodynamic modelling utilising the MTDATA software package and a conceptual model of the interfacial mineral layer. The main conclusions drawn from this project were:

1. A mineral layer formed at the coke/iron interface during coke dissolution into liquid iron. Within the experimental temperature range of 1450-1550°C, the mineral layer was solid and persistent at the interface. The
amount of mineral matter present in the mineral layer was observed to be increasing with increased reaction time. The composition and structure of the mineral layer changed with both experimental time and temperature.

2. The kinetics of carbon dissolution from the coke to the liquid iron were dependant on the structure of the interfacial mineral layer. The mineral layer formed at the coke iron-interface during coke dissolution was at least in part rate controlling the coke (carbon) dissolution reaction for the coke-iron system studied.

3. The composition of the mineral layer was principally composed of oxides of aluminium and calcium, present as various calcium aluminates and calcium sulphides. Initially the mineral layer was a loose agglomeration of particles of which a majority were alumina particles. As the dissolution reaction proceeded, the loose agglomeration of particles was replaced by an open acicular layer that was predominantly the CA6. As the dissolution reaction continued further, the calcium aluminates became increasingly richer in calcium oxide, with the predominate phase present in the mineral layer progressing through the calcium aluminates from CA6, to CA2 to CA. The apparent calcium enrichment of the mineral layer was observed to occur more rapidly as the experimental temperature increased.

4. The morphology of the mineral layer was observed to change from an initial loose agglomeration of particles, to an open acicular structure to a dense layer as the dissolution reaction proceeded. The observed change in the morphology of the mineral layer was directly related to compositional changes occurring in the mineral layer. In layers where the predominate phases were the acicular CA6 phase and the tabular CA2 phase the mineral layer had an open porous structure. In layers where the predominate phase was CA or significant amounts of CaS had formed, the layer had a dense structure.
5. The composition of the sulphide layer observed to form at the iron side of the coke/iron interface indicated that it was principally a calcium sulphide layer. It was found that the formation of the calcium sulphide layer was preceded by the formation of the calcium aluminate layer. Only after the calcium aluminate layer had experienced progressive calcium enrichment and the CA and CA2 phases had formed did the CaS phase appear at the iron interface. Thermodynamic analysis of the experimental results confirmed that the formation of the calcium enriched calcium aluminates, CA2 and CA, were a necessary requirement to stabilise the calcium sulphide layer for the coke composition studied.

6. A coke analogue for use in dissolution studies was developed. Multiple forms of carbon are present in the coke analogue. Carbon is present in the form of graphite, glassy carbon and carbon precipitated on the pore walls. It was found that the dissolution behaviour of the coke analogues in liquid iron was graphite in liquid iron indicating a carbonaceous structure that is significantly different from graphite has been achieved in the coke analogues. When single phase calcium aluminates were introduced into the coke analogues, calcium enrichment of the resulting calcium aluminate mineral layer was observed. The observed carbon dissolution kinetics were dependant on the structure of the interfacial calcium aluminate layer. Consistent with the coke dissolution studies, the calcium aluminate layer formed at the coke analogue iron interface during carbon dissolution was at least in part rate controlling the carbon dissolution reaction for the coke analogues studied.

7. Utilising the sessile drop experimental technique the wettability with liquid iron-carbon-sulphur alloys of the predominate phases that were observed in the mineral layer were measured. It was observed that the contact angle decreased as the proportion of lime (CaO) in the calcium aluminate increased. Further it was observed that while the presence of sulphur in the melt increased the contact angle for the alumina and CA6
substrates, on the CA2 and CA substrates the contact angle was decreased. The improvement in the wetting of the CA2 and CA substrates with sulphur was attributed to the formation of CaS at the substrate/droplet interface.

In conclusion, a detailed study on the effect of the mineral layer that forms at the coke/iron interface during coke dissolution into liquid iron has been conducted. This study has produced new fundamental data on the growth and development of the mineral layer and the wettability of the predominate calcium aluminates observed in the mineral layer. These detailed studies have illuminated the changing nature of the layer in terms of both composition and morphology and found that the kinetics of carbon dissolution from the coke to the liquid iron were dependent on the structure of the interfacial mineral layer.

The coke used in this study was produced from a blend of “typical” Australian Illawarra coals. Such coals are relatively high in quartz, low in sulphur while the CaO content could be described as mid range. While the coke analogue provided a controlled method allowing the mineral layers growth and development to be replicated, a natural extension of this work would include a study of cokes with different ash chemistries. Such a study would allow a fuller picture of how the mineral layers growth and development is influenced by coke mineral matter.

The question of calcium enrichment of the mineral layer is also unanswered by this study. A number of possible explanations for the observed calcium enrichment of the mineral layer are offered, but the author is unable to distinguish between the different mechanisms. Further work in this area, potentially utilising the coke analogues, may clarify the source and mechanism of calcium enrichment of the mineral layer, further adding to the emerging complex picture that is the role that coke mineral matter plays in coke dissolution.
In an industrial context, the question of whether the interfacial mineral layer persists and develops at the interface is an important one. If the mineral layer comes into contact with blast furnace slag it is likely the layer will be dissolved or modified by the slag. However, if the mineral layer is formed in the absence of a slag phase, as would be the case in the blast furnace hearth, beneath the slag level, the mineral layer could persist and develop. The change in the coke dissolution rate as a result of the formation and changes of the mineral layer would be expected will affect carbon pickup and thus coke utilisation within the blast furnace.