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Investigations on the anomalous oxidation behaviour of high-carbon gas-based direct reduced iron (DRI)

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Abstract

Sponge iron or direct reduced iron (DRI) often shows a tendency to spontaneously combust in a moist oxygen-containing atmosphere. This tendency, however, is different for gas-based DRI compared with coal-based DRI. In this paper the unique oxidation behaviour of gas-based DRI is discussed and has been compared with the combustion behaviour of coal-based DRI.

Keywords: Anomalous oxidation; Coal-based DRI; Direct reduced iron (DRI); High-carbon gas-based DRI; Sponge iron; Spontaneous combustion

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1. Introduction

Direct reduced iron (DRI) or sponge iron has the inherent characteristics of pyrophoricity and reoxidation to its oxide because of its extremely high surface-to-volume ratio and poor thermal conductivity. The pyrophoric nature of sponge iron has created many fire hazards during its transportation and shipping. The subject has been thoroughly investigated by the present authors and others [1–14]. Its mechanistic and industrial implications have also been published.

It is well known that two basic types of DRI are produced. The majority of the DRI is produced by the solid-state reduction of iron ore using reformed natural gas as the reductant in a shaft furnace. The other process uses non-coking coal as reductant, reduction usually being performed in a rotary kiln at around 1000°C. Investigations

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have revealed that these DRI have different characteristics in respect of their stability and tendency towards reoxidation [15]. Substantial claims have been made by some suppliers of DRI, especially HyL Iron and Steel Technology, Mexico, that the DRI produced by their technology is inherently resistant to reoxidation, thus enabling its storage for long periods and its safe and reliable transportation [16]. It has been stated that one of the main reasons for greater stability of this type of DRI is its higher carbon content (1.8–2.3%). The greater amount of carbon present, especially as cementite, gives the product greater stability against reoxidation up to 150°C. This is because in a pellet containing 2.3% carbon, over 31% of the weight is cementite and iron carbide is inherently less prone to oxidation than free metallic iron.

It has been claimed [16] that in HyL pellets the carbon is concentrated around the external surface, forming a protective shell against reoxidation. The concentration of carbon decreases towards the centre of the pellet so that about 80% of the carbon is in the shell which is about 2 mm thick. Fig. 1 shows a typical distribution of the carbon in the DRI pellet.

Investigations have revealed that depending on the temperature of the environment, the DRI product will have varying degrees of stability. These stability zones are presented in Fig. 2. As observed from Fig. 2, the zone of instability starts beyond 200°C. The nature and mechanism of DRI reoxidation beyond 200°C is, however, still not known. This paper attempts to answer some of these questions.

2. Experimental

2.1. Materials

DRI containing about 1.9% carbon, produced by the HyL process, has been used in the present investigations. The composition of the sample is given in Table 1.

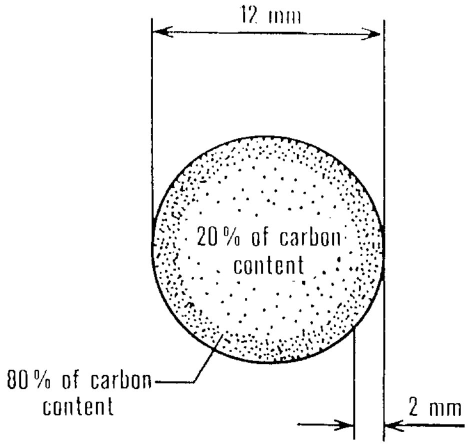

Fig. 1. Typical distribution of carbon in HyL DRI pellet.

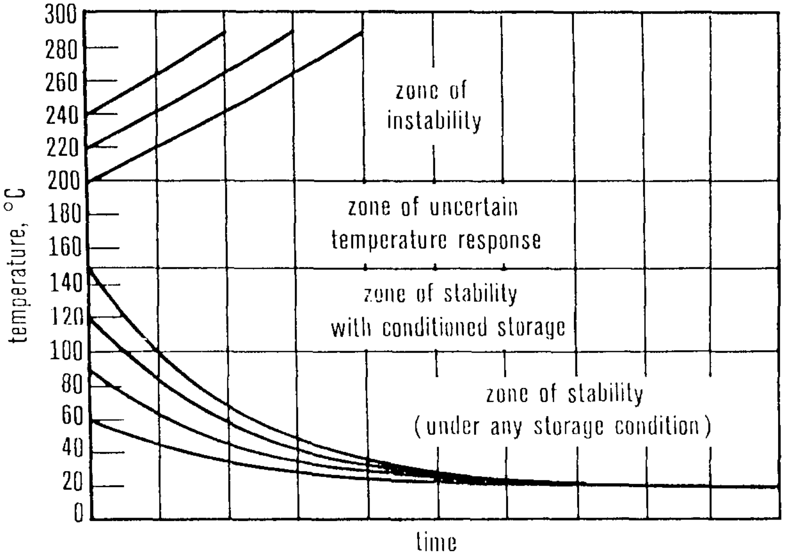

Fig. 2. Stability zones of HyL DRI product.

Table 1
Composition of direct reduced iron (in mass percent)

Constituents	Gas-based HyL DRI
Fe (total)	86.9
Fe (metal)	79.2
Degree of metallization (DOM)	91.1
FeO	8.7
Fe_2O_3	1.4

2.2. Procedure

The equipment consisted of a vertical furnace, a ceramic tube reaction chamber housing the sample holder, a gas inlet pipe and thermocouples (Fig. 3). The temperature of the furnace was controlled by means of an electronic two-step controller. A perforated platinum basket (3 cm long and 1 cm diameter) was suspended from a single-pan Mettler electronic balance with a readability of 0.1 mg using a Kanthal chain link. The balance could weigh up to 160 g. Purified air or nitrogen was supplied to the reaction chamber through a metering arrangement. The oxidizing conditions were controlled by supplying carefully cleaned and dried air to the reaction chamber at a controlled and measured rate.

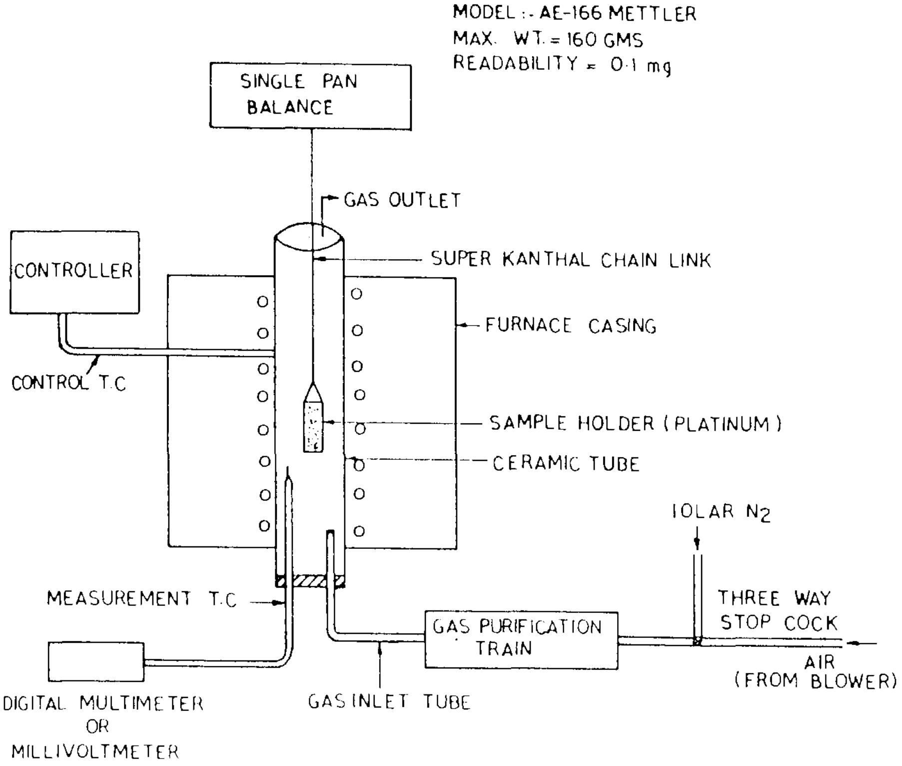

Fig. 3. Schematic diagram of the thermogravimetry equipment.

The furnace was initially heated to the desired temperature and the reaction chamber was flushed with purified (IOLAR grade) nitrogen. Nitrogen flushing created an inert atmosphere during the heating up period. The pre-weighed sample was suspended in the reaction chamber by the chain and basket and heated to the reaction temperature. Any minor changes in the weight during this heating-up period was ignored.

Preliminary trials showed that beyond a linear gas velocity of about 15 mm s^{-1}, the reaction rate became independent of the gas flow rate. Similar values of gas velocity were also obtained by other investigators while studying the oxidation behaviour of DRI [17]. Hence the air flow was maintained above this flow rate in all subsequent experiments to eliminate the influence of gas-phase diffusion. After allowing sufficient time for the sample to attain the furnace temperature the nitrogen flow was stopped and air flow started. The changes in weight with time were then recorded and used to analyse the primary kinetic data (α-t plots) and to obtain insight into the reaction mechanism.

3. Results and discussion

In the present analysis the residual oxygen in the sample was neglected since it originated from iron oxides in the unreduced form, and not from fresh oxidation. It is expected that the unreduced oxide was present as a dense retained wustite which is relatively inaccessible to the gas phase. Thus its behaviour and effect on the reoxidation process is likely to be totally different from the fresh oxide forming on reduced metallic iron and it should logically be disregarded.

The fractional conversion (α) was defined as:

$$\alpha = \frac{\text{Amount of oxygen taken up by sponge iron}}{\text{Amount of oxygen required to convert the iron and its oxides in sponge iron to } Fe_2O_3}$$

Fig. 4 presents the primary kinetic plots (α vs t plots) obtained from the continuously recorded weight gain data during isothermal reoxidation of DRI. Previous investigations [3, 6] by the authors with DRI samples have shown that the reoxidation process follows a first order law. The reduced time plot technique [6] was used for elucidation of the oxidation mechanism. In view of the above, the integrated form of the first order law i.e. $G(\alpha) = -\ln(1-\alpha)$ was plotted against time for the primary kinetic data obtained at 665 K (Fig. 5). The excellent linearity of the plot shows that the gas-based DRI oxidation also follows a first order law.

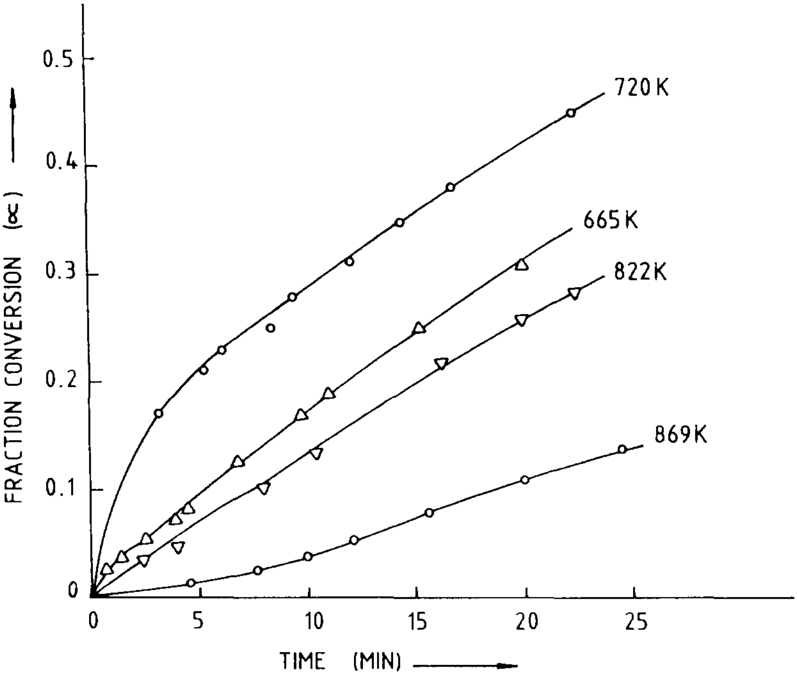

Fig. 4. Primary kinetic plots for oxidation of gas-based HyL DRI.

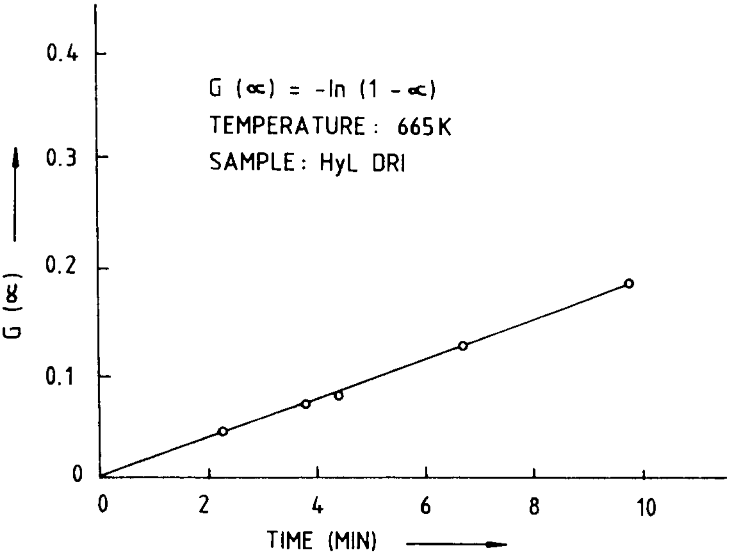

Fig. 5. First order plot to linearise kinetic data for oxidation of HyL DRI.

Closer examination of the primary kinetic plots (Fig. 4) shows a surprising trend, however, namely that reoxidation rates are less pronounced at higher temperatures. This unexpected finding can be attributed to the special feature of the HyL DRI sample, i.e. the higher carbon content.

Because of the presence of free and combined carbon, the oxidation reactions should produce CO_2, CO and oxides of iron. As per the Ellingham diagram, carbon cannot reduce Fe_2O_3 to iron at lower temperature regimes than those used in the present work; oxidation of iron cannot, therefore, be prevented. However, iron oxidation would certainly be impeded both by thermodynamic and kinetic factors. Banerjee et al. [18] have shown that effective oxidation of carbon begins at about 723 K which coincides with the reversal of α–t plots shown in Fig. 4. This seems to indicate that the anomalous trend is because of carbon oxidation. Oxidation of carbon, both combined and free, in the outer layer, would be more pronounced at higher temperatures. Presumably the gases evolved envelope the DRI particles and impede atmospheric reoxidation of DRI, the effect being more pronounced as the temperature is raised. In contrast, in the case of coal-based DRI, with increase in temperature the α-t plot is raised as shown in Fig. 6. It is not possible to perform meaningful analysis of the kinetic data because of the uncertainties concerning the nature of the isothermal experimental data above 720 K. However, non-isothermal oxidation studies carried out with HyL DRI in the temperature range 30°–1200°C and at a heating rate of 15°C min^{-1} have shown that the sample has a non-isothermal activation energy value (E) of 55 kJ mol^{-1} and a pre-exponential factor (A) of 79 (Fig. 7). This E value can be compared with a non-isothermal E value of 21 kJ mol^{-1} for a coal-based DRI (Fig. 8). The differential approach was used in these analyses [19].

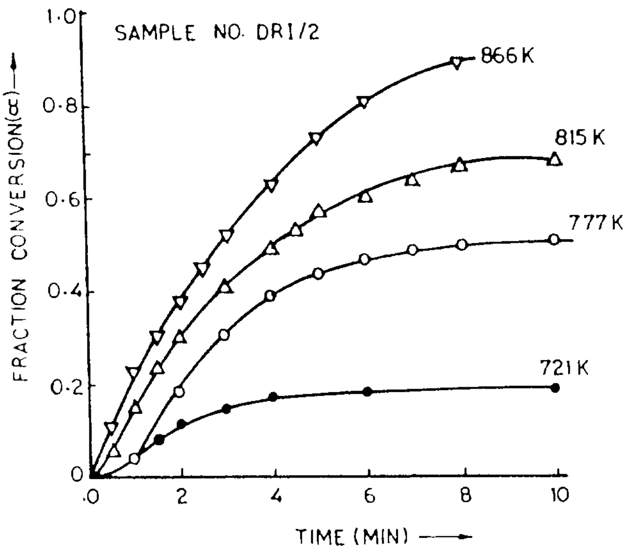

Fig. 6. Primary kinetic plots for oxidation of coal-based DRI.

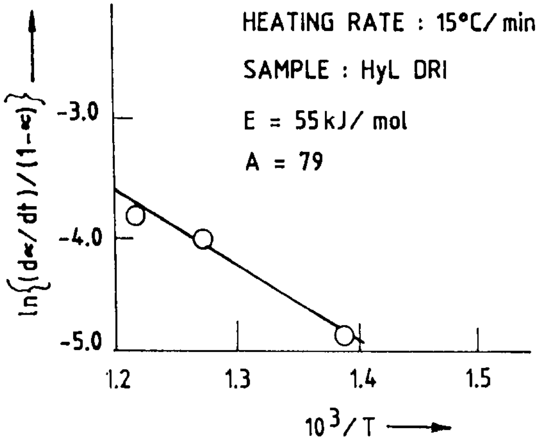

Fig. 7. Differential plot for gas-based HyL DRI.

4. Conclusions

Thermogravimetric techniques have been used to elucidate the mechanism and gain detailed insight into the anomalous oxidation behaviour of high-carbon gas-based DRI. For this type of DRI the non-isothermal E value lies around 55 kJ mol^{-1}

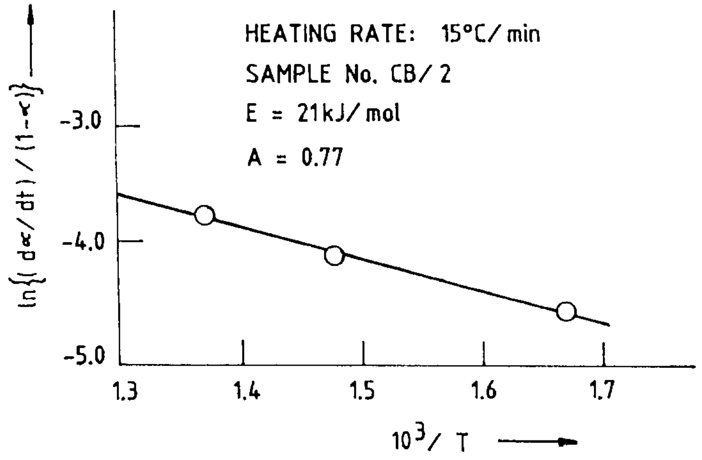

Fig. 8. Differential plot for coal-based DRI.

compared with 21 kJ mol^{-1} for a coal-based DRI. The gas-based DRI oxidises relatively more quickly at lower temperatures, around 720 K, but at elevated temperatures, above 800 K, the rate of oxidation slows down, presumably because of simultaneous oxidation of carbon.

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