

Determination of kinetic parameters for the reoxidation of direct reduced iron under rising temperature conditions

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Abstract

This paper presents the main kinetic parameters for the reoxidation of direct reduced iron (DRI) samples in air under non-isothermal conditions and compares the data with isothermal kinetic parameters for a typical DRI sample. It is found that the non-isothermal activation energy (ΔE) values are less than the isothermal ΔE values. For coal based DRI, the non-isothermal ΔE values lie in the range 20–35 kJ mol⁻¹. For gas based DRI the value is much higher, about 55 kJ mol⁻¹. For the reoxidation of DRI, the kinetic compensation effect (KCE) has been found to be valid.

INTRODUCTION

During the last decade, considerable attention has been paid to the problem of spontaneous ignition of sponge iron or direct reduced iron (DRI) in moist oxygen-containing atmospheres [1, 2]. The problem often leads not only to loss of the metallic part of the material but also to fire hazards and consequent damage to the storage area or the vehicle carrying the DRI cargo, such as a ship, railroad car etc. [3, 4]. It is interesting to note that this process of spontaneous combustion of sponge iron is very similar to that of coal, and is a typical example of a naturally occurring non-isothermal process, whereby the heat generated by the low temperature oxidation of DRI fails to be dissipated and leads to hot spot generation within the DRI pile.

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Subsequently, beyond about 300°C, spontaneous combustion takes place [5]. The present authors have reported the kinetic parameters for the above process under isothermal conditions for the reoxidation of DRI [6]. However, not much information is available about the kinetic parameters under non-isothermal conditions. This paper therefore presents the major kinetic parameters for reoxidation of typical DRI samples and compares the kinetic parameters for one DRI sample under isothermal and non-isothermal conditions.

EXPERIMENTAL

Non-isothermal studies on the oxidation of DRI were carried out in static air in order to obtain the thermogravimetric data. A Netzsch STA-409 model simultaneous thermal analyser was used. The chemical compositions of different DRI samples used in the studies are given in Table 1.

TABLE 1
Compositions of DRI used

Constituents	Sample			
	CB/1 ^a	CB/2 ^a	HBI	HyL
Fe (total)	82.16	85.78	93.08	86.89
Fe (metal)	63.43	71.53	89.29	79.19
DOM	77.20	83.38	95.92	91.14
FeO	22.58	16.53	1.38	8.65
Fe ₂ O ₃	1.66	1.99	3.87	1.39

^a CB stands for coal based DRI.

Procedure

The experiments were carried out using –170 mesh size DRI powder obtained after pulverizing the DRI sample. The sample mass used for oxidation studies was ≈60 mg. Such fine grain size was used to obtain a representative sample while conducting experiments with small quantities of sample. Static air was used to eliminate any possibility of sample ejection by air, and also bearing in mind that the reoxidation of DRI in static air is more akin to the actual spontaneous combustion process. In the experiments alumina was generally used as the reference material.

The maximum temperature was kept at 1200°C and the heating rate was chosen in the range 5–20°C min⁻¹. However, most of the samples were tested at 15°C min⁻¹ heating rate. Extensive studies were carried out with one coal based DRI sample (Sample No. CB/1), and the comparison of

isothermal and non-isothermal kinetic parameters was effected with data obtained from experiments conducted with this sample.

RESULTS AND DISCUSSION

In the analysis that follows, the fractional conversion (α) has been defined disregarding the residual oxygen content of DRI. This was done because the oxygen already present in the sample is probably due to the unreduced form of iron oxide and not to fresh oxidation. It is considered that the unreduced oxide is present as dense retained wustite, which is relatively inaccessible to the gas phase. Thus its behaviour and its effect on the oxidation process are likely to be totally different from those of the fresh oxide forming on reduced metallic iron. Hence the FeO present at the start should logically be disregarded for defining α . This assumption can also be justified from the chemical analysis of the DRI used in the investigation. Table 1 shows that the DRI samples contain FeO in the range 1.4–22.6%.

For the analysis of the kinetic data two integral methods, those given by Ray and Dixit [7] and by Coats and Redfern [8] were used. The values obtained have been compared with the data obtained by the differential method [9]. Figure 1 presents the primary kinetic plots (α vs. t) obtained from the continuously recorded weight gain data during the non-isothermal reoxidation of a coal based DRI (Sample No. CB/1) at four different heating rates in the range 5–20°C min⁻¹. The results show that the α – t plots shift to the right with decrease in the heating rate. This may be attributed

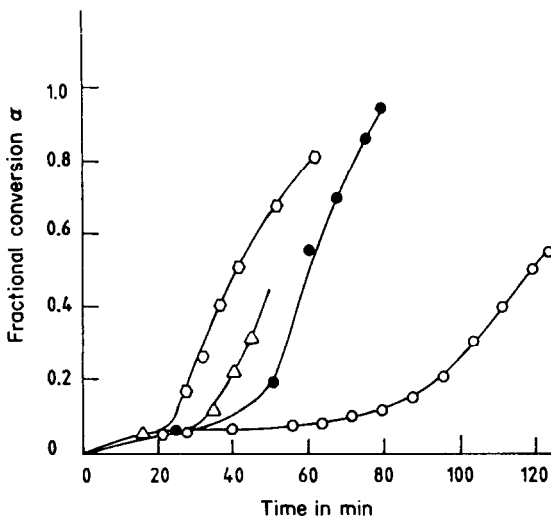


Fig. 1. Primary kinetic plot for the oxidation of a coal based DRI (Sample No. CB/1): ○, 5 K min⁻¹; ●, 10 K min⁻¹; △, 15 K min⁻¹; ○, 20 K min⁻¹.

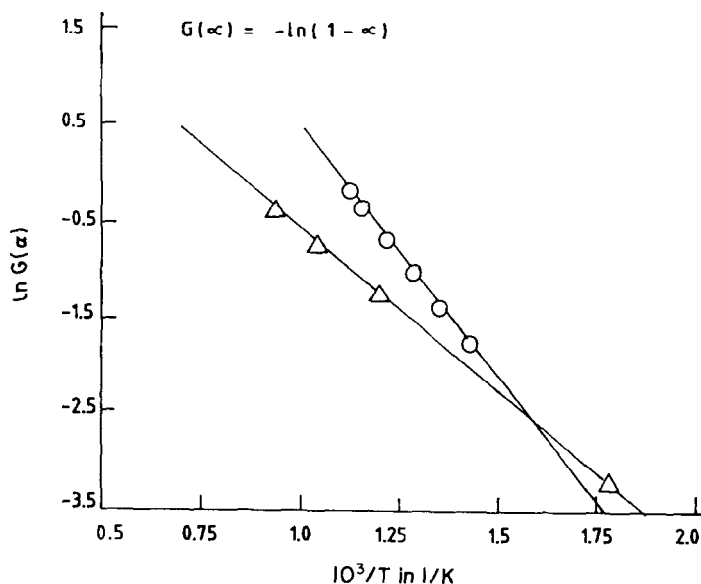


Fig. 2. Dixit and Ray's plot for a coal based DRI (Sample No. CB/1): ○, 5 K min⁻¹; Δ, 20 K min⁻¹.

to the fact that, when the heating rate is higher, the system attains higher temperature sooner and, therefore, in a given time there is more reaction. Figure 2 shows two typical plots of data for 5 and 20°C min⁻¹ rates of heating according to the Ray and Dixit equation [7]. The integrated form of the rate expression, i.e. $G(\alpha) = -\ln(1 - \alpha)$, has been used, based on the results of the isothermal studies carried out on the DRI sample [6]. The plots in Fig. 2 are linear and the slopes provide the activation energy values. For different heating rates the slopes are different, indicating that the activation energies differ for different rates of heating. The apparent activation energy values calculated from the slopes are summarized in Table 2. It is seen that the deviation from the isothermal ΔE value increases with increase in heating rate. If it is assumed that the deviation arises from

TABLE 2

Activation energy data from Dixit and Ray's plot

Serial No.	Heating rate/°C min ⁻¹	Activation energy/kJ mol ⁻¹
1	5	44
2	10	40
3	15	33
4	20	29

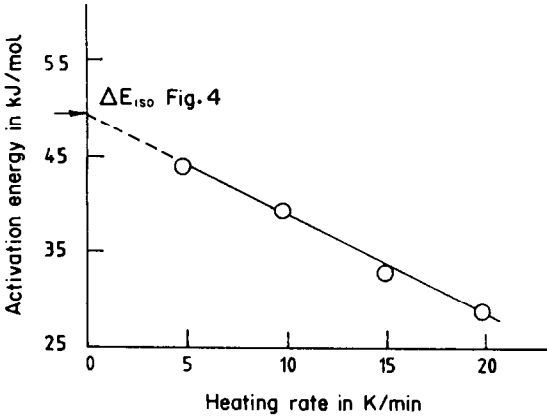


Fig. 3. Plot of apparent activation energy values [7] vs. heating rate.

thermal non-equilibrium in the sample mass, then the correct ΔE value should be obtainable by extrapolating to zero heating rate. Figure 3 shows a plot of the apparent ΔE values versus heating rate. It is found that the extrapolated value is indeed close to the isothermal ΔE value of 50 kJ mol^{-1} obtained for this DRI (Fig. 4). The apparent ΔE values have been also obtained using the Coats and Redfern equation and the differential approach. The plots are shown in Figs. 5 and 6. It is again observed from these plots that the apparent ΔE values change with heating rate. Table 3 summarizes the variation for both the approaches. The pre-exponential factor A may be calculated by the method discussed below.

We have

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp(-\Delta E/RT) dt \tag{1}$$

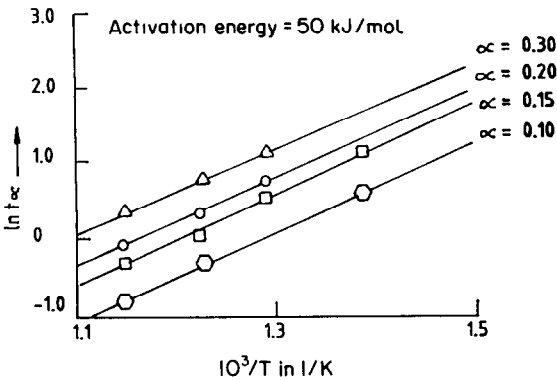


Fig. 4. Differential plots for oxidation of DRI under isothermal conditions (Sample No. CB/1).

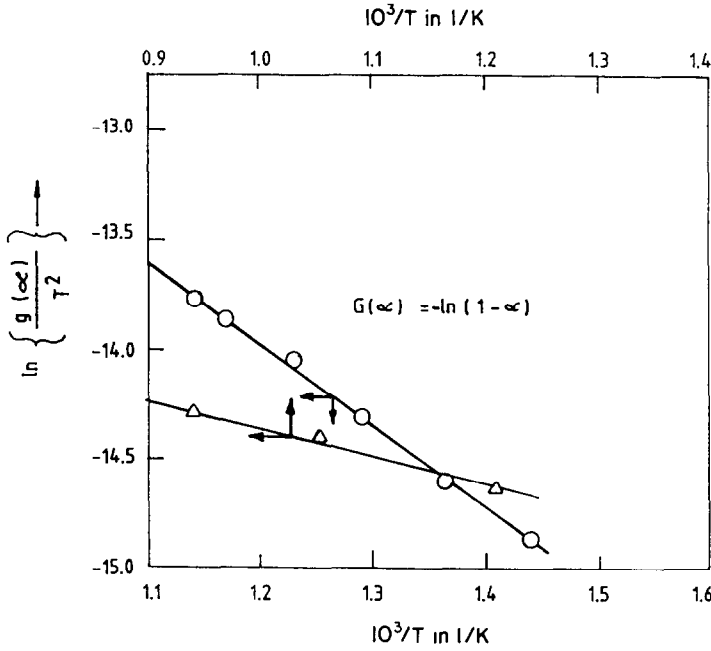


Fig. 5. Coats and Redfern Plot for a coal based DRI (Sample No. CB/1): ○, 5 K min⁻¹; Δ, 20 K min⁻¹.

Transposing, we have

$$A = g(\alpha) / \int_0^t \exp(-\Delta E/RT) dt \tag{2}$$

The right hand side (RHS) integral is obtained by first plotting $\exp(-\Delta E/RT)$ values at instantaneous values of time and then integrating by graphical means or using Simpson's one-third rule [10]. Then the $g(\alpha)$

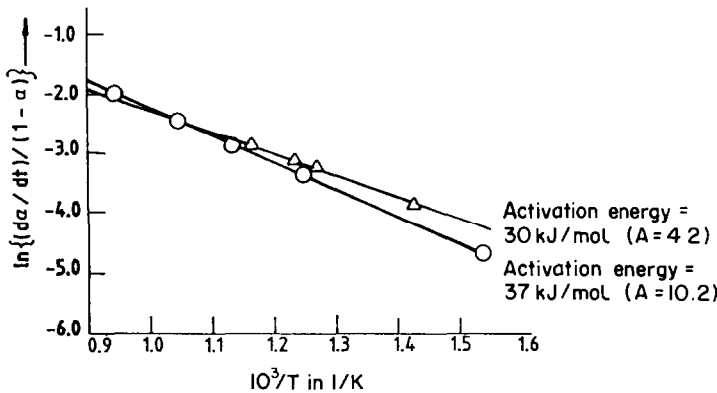


Fig. 6. Differential plots for a coal based DRI (Sample No. CB/1): ○, 10 K min⁻¹; Δ, 20 K min⁻¹.

TABLE 3

Summary of activation energy data from Coats and Redfern and differential plots

Serial No.	Heating rate/ $^{\circ}\text{C min}^{-1}$	Activation energy/ kJ mol^{-1}	
		Coats and Redfern	Differential
1	5	31	39
2	10	21	37
3	20	16	30

value at time t is calculated from the α value shown in the $\alpha-t$ plot. The value of $g(\alpha)$ is then divided by the RHS integral to obtain the value of A . A typical value of the pre-exponential factor is shown in Fig. 6. Some other A values are also given, along with the plots for the determination of activation energy. It should be noted that, although in theory the differential approach is the most accurate, it suffers from uncertainties as regards to the calculation of slopes. It is therefore not possible to say which approach provides the most accurate data. Moreover, closeness to the isothermal value may not be the deciding factor, because non-isothermal ΔE values are known to differ from the isothermal values [11]. However, if the differential approach yields a straight line, the linearity indirectly implies that the values of the slopes are reasonably accurate. Therefore, if linear plots are obtained from differential plots, then this approach should be the best.

As discussed earlier, the combustion of sponge iron in a pile is a non-isothermal process. Thus, non-isothermal data may be considered

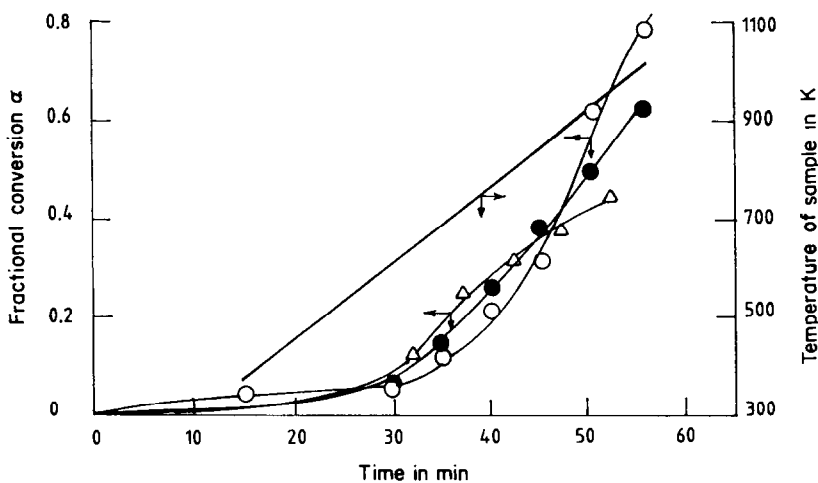


Fig. 7. Primary kinetic plots for various DRI samples: ●, coal based DRI (CB/2); △, HyL DRI; ○, hot briquetted iron (heating rate 15 K min^{-1}).

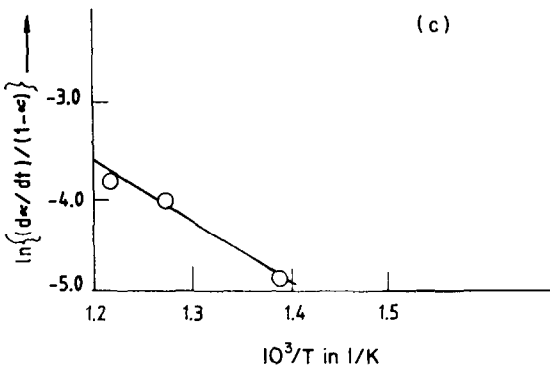
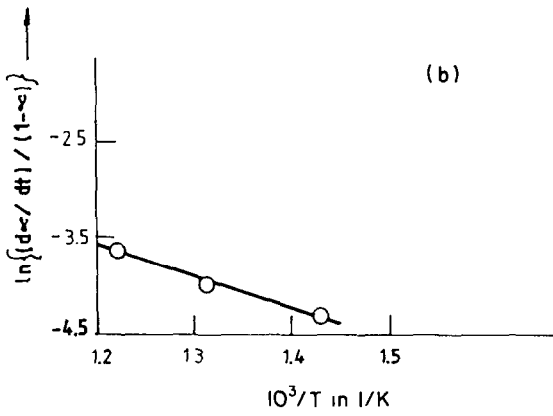
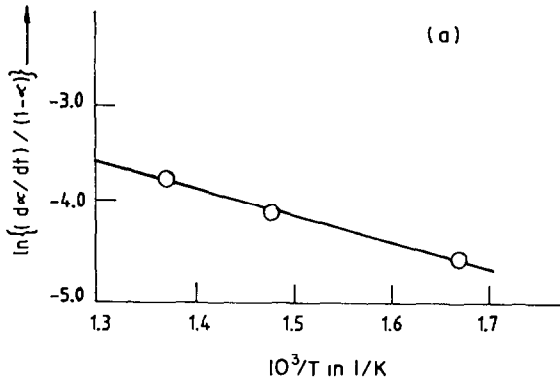


Fig. 8. Differential plots for various DRI samples; heating rate 15 K min^{-1} . (a) CB/2; activation energy 21 kJ mol^{-1} ; $A = 0.77$. (b) Hot briquetted iron; activation energy 28 kJ mol^{-1} ; $A = 1.52$. (c) HyL DRI; activation energy 55 kJ mol^{-1} ; $A = 79$.

more meaningful for understanding the phenomenon of spontaneous combustion due to reoxidation of DRI. However, small samples such as those used the TG studies cannot indicate the combustion behaviour of an actual sponge iron pile because of the different nature of heat dissipation in the former.

Non-isothermal reoxidation of some other types of DRI sample has also been studied. In these cases, however, the heating rate was fixed arbitrarily at $15^{\circ}\text{C min}^{-1}$. Figure 7 shows the $\alpha-t$ plots for the samples from three different processes. It is observed that the samples can be arranged in the following decreasing order of reactivity: (1) hot briquetted iron (HBI); (2) coal based DRI; (3) gas based DRI.

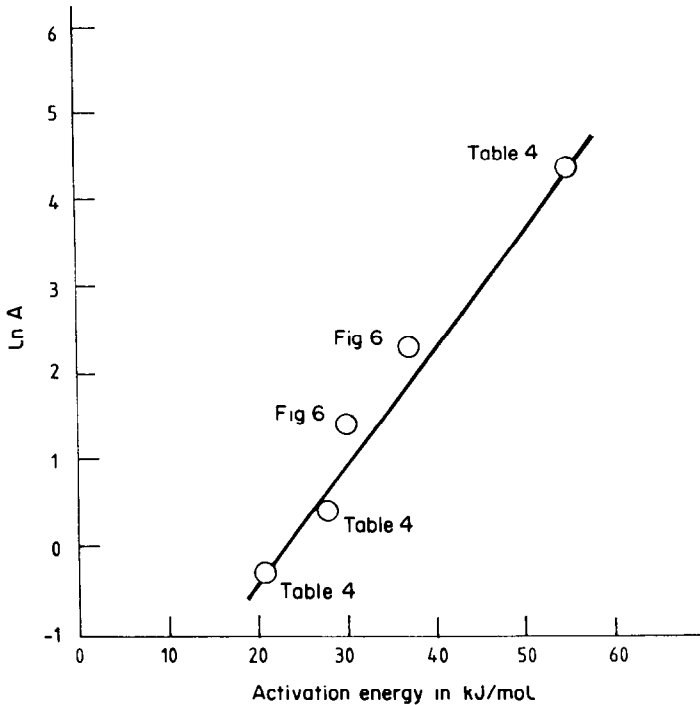


Fig. 9. Kinetic compensation effect (KCE) for the reoxidation of DRI.

TABLE 4

Activation energy and pre-exponential factors of DRI samples under non-isothermal conditions: determined by differential approach (heating rate $15^{\circ}\text{C min}^{-1}$)

Sample type	Activation energy/ kJ mol^{-1}	Pre-exponential factor
Coal based DRI (Sample No. CB/2)	21	0.77
Hot briquetted iron	28	1.52
HyL DRI	55	79

The differences in reactivity are due to a number of factors. For example, in the case of the gas based DRI sample, reoxidation is impeded by the presence of a higher amount of carbon. Hot briquetting reduces the reactivity of large particles because the briquetting process closes some pores. However, this effect would not be visible when studying the oxidation kinetics of fine particles. Figure 8 shows the plots for three DRI samples drawn according to the differential approach. The apparent ΔE values calculated are also indicated. In the case of the second coal based DRI (Sample No. CB/2), the ΔE value from the non-isothermal run (21 kJ mol⁻¹) is substantially smaller than the corresponding isothermal ΔE value (35 kJ mol⁻¹). A similar trend has also been found in the case of the first coal based DRI (Sample No. CB/1). This is probably because of the previously discussed possibility of thermal non-equilibrium. Table 4 lists some of the activation energies and pre-exponential factors determined by the differential approach.

Kinetic compensation effect

It is now well established that a linear relationship exists between $\ln A$ and ΔE for many thermally activated processes under different experimental conditions. The phenomenon called the “kinetic compensation effect” (or KCE) generally applicable for thermal decomposition processes states that a linear relationship exists between ΔE and A as follows under varying experimental conditions

$$\ln A = a + bE$$

In the case of reoxidation of DRI also the KCE holds good (Fig. 9); the linear relationship can be given as

$$\ln A = -3.044 + 0.137E$$

and the regression coefficient R obtained for the plot is 0.985.

CONCLUSIONS

1. Activation energy values of DRI were determined by both integral and the differential approach. It has been concluded that the value of ΔE obtained by the differential approach is likely to be the more accurate. The non-isothermal ΔE values have been found to be lower than the isothermal ΔE values, presumably because of thermal non-equilibrium during non-isothermal studies.

2. For coal based DRI and HBI, the non-isothermal ΔE values lie in the range 20–35 kJ mol⁻¹. For HyL DRI, however, the non-isothermal ΔE

value is much higher and is around 55 kJ mol^{-1} . Since most of the cases of spontaneous combustion of DRI are non-isothermal in nature, non-isothermal ΔE values should be considered more meaningful for the analysis of actual data.

3. The DRI samples having higher non-isothermal ΔE values are less susceptible to spontaneous combustion.

4. The kinetic compensation effect is found to be valid for reoxidation of direct reduced iron.

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