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APPLICATION OF THERMAL ANALYSIS TO STUDY SMELTING REDUCTION KINETICS

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Abstract

A thermal analysis study on the reduction of iron oxide rich slags under different conditions is presented in this paper. The effects of important process variables such as time, temperature, lime–silica ratio, FeO level in slag etc. are discussed. It is shown that the mechanism of reduction by externally added graphite is different from that by a carbon saturated bath although the activation energy values are similar.

Keywords: kinetics, reduction, slag reduction, smelting reduction, thermal analysis

Introduction

In recent years, smelting reduction has gained increasing importance as a possible alternative to the blast furnace process to produce hot metal. It is likely to prove superior to the conventional route on the basis of productivity, capital investment, flexibility over process control and flexibility as regards raw materials. Essentially, smelting reduction consists of two major steps: (a) pre-reduction of iron bearing raw materials in solid state and (b) subsequent smelting of the pre-reduced iron ore in liquid slag phase. In the DR-EAF route of ironmaking, most of the oxygen has to be removed in the solid state itself and the second step essentially consists of melting along with some refining reactions. In smelting reduction, on the other hand, oxygen is only partially removed in the solid state and the rest is removed in the liquid state through slag phase reduction. In addition, there is great emphasis on utilisation of the heat value from the off gases.

The reduction of iron oxide rich slags is the most important aspect of smelting reduction. Iron oxide in the slag phase is presumably reduced by carbon mainly through a gaseous intermediate as per the following scheme [1, 2]:

$$FeO + C = Fe + CO \qquad (1)$$

$$FeO + C = Fe + CO_2 \qquad (2)$$

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$$CO_2 + C = 2CO \tag{3}$$

There is a good deal of literature on smelting reduction kinetics and different workers have employed different experimental techniques in their studies. The techniques employed include chemical analysis [3, 4], thermogravimetry (TG) [5–7], evolved gas analysis (EGA) [8–15], etc. However, nearly all experimental data reported so far suffer from various uncertainties. There have been problems with reaction of slag with the crucible material. Even recrystallized alumina reacts with liquid iron oxide bearing slags to form a solid spinel which changes the melt viscosity and ultimately affects reaction kinetics. Platinum metal also reacts with such slags. A graphite crucible, as expected, is likely to react even more vigorously with slags. In addition, there are uncertainties regarding reaction interface area due to foaming of slag, chemical analysis of slag and sampling procedure etc.

In the present study a TG set up fabricated in the laboratory has been used to monitor the change in weight during reduction. The reductant was either solid carbon added as graphite or carbon dissolved in a carbon saturated iron bath. It is assumed that the product gas is only CO and thus one can easily estimate the degree of FeO reduction from the weight loss data.

Experimental

FeO was prepared by fusing the stoichiometric mixtures of Fe_2O_3 and pure iron powder at 1300°C in a neutral atmosphere. This FeO and pure CaO and SiO_2 were fused to prepare synthetic slags. Carbon saturated iron bath was prepared by dissolving graphite in iron powder kept at the experimental temperature. The TG set up was assembled by placing a direct reading digital electronic balance (Sartorius model A120S, max. load 120 g, readability 0.1 mg) over a resistance heated vertical tube furnace. A graphite crucible containing slag and reductant was suspended from the bottom of the balance and placed in the hot zone in a stream of inert gas. The weight change due to reduction was continuously measured. The degree of reduction at time t was expressed using the following expression:

$$\alpha = \frac{FeO_i - FeO_t}{FeO_i} \tag{4}$$

where, FeO_i and FeO_t are respectively the initial value of FeO concentration and concentration at time t.

Results and discussion

Figure 1 shows the effect of temperature on reduction of an iron oxide rich slag by carbon saturated iron bath. All the data fit into a first order kinetic equa-

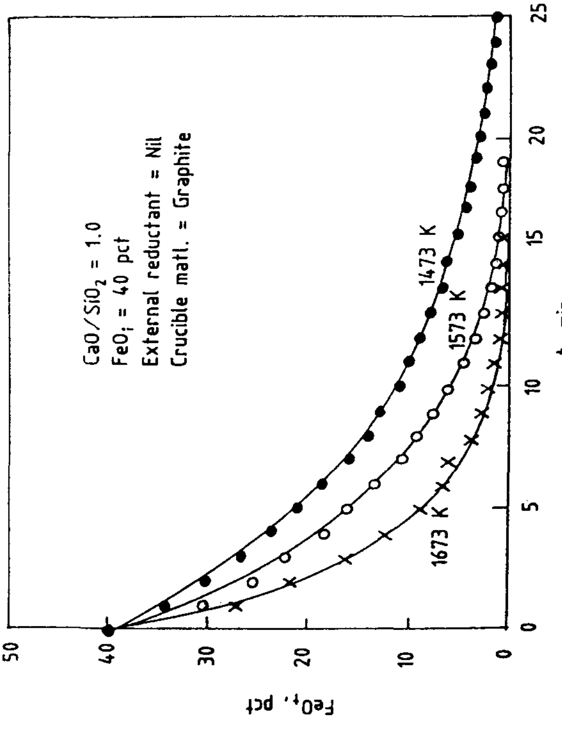

Fig. 1 Effect of temperature on slag reduction

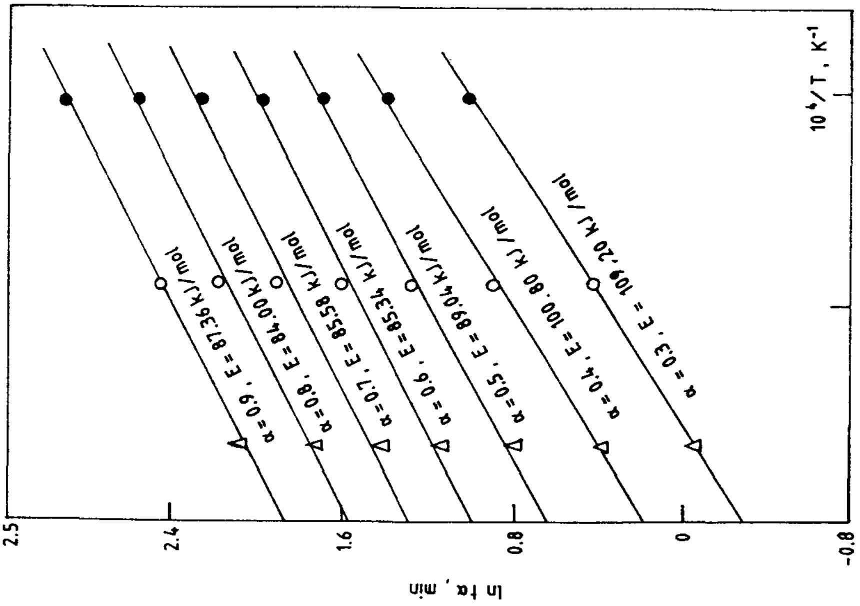

Fig. 2 Analysis of data by differential method

tion. These data have been analysed by a differential method as shown in Fig. 2. The Arrhenius plot i.e. the integral approach also gives a straight line. An activation energy value of 85 kJ/mol is obtained by the integral approach whereas the same obtained through the differential approach lies within 84–109 kJ/mol. Figures 3 and 4 illustrate some typical results which indicate that the reaction is aided by increase in CaO/SiO_2 ratio upto 1.5 and increase in initial FeO concentration level. In all these experiments the source of reductant is primarily the graphite saturated pig iron, the crucible itself also playing a minor role. All the results follow first order kinetics.

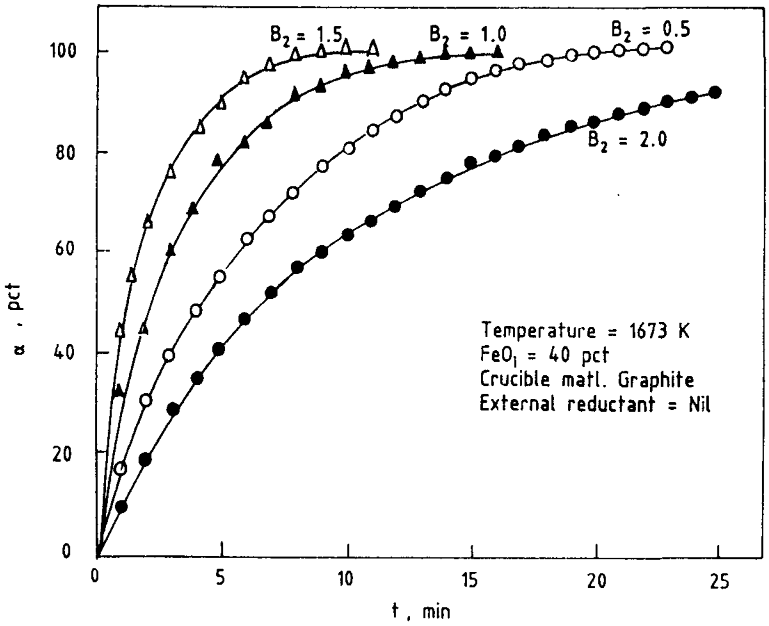

Fig. 3 Effect of lime–silica ratio on the reduction kinetics

If solid particles of graphite are used as reductant instead of a carbon saturated iron bath then the $\alpha - t$ plots follow a different trend as shown in Fig. 5. The sigmoidal plots are typical of nucleation and growth model. Here the graphite particles, distributed throughout the slag mass, act as nuclei for heterogeneous nucleation and there is nucleation delay. The plots follow the Johnson-Mehl (J-M) type equation which has the following form

$$\frac{d\alpha}{dt} = k^n t^{n-1} (1 - \alpha) \qquad (5)$$

where, k and n are constants.

The value of the exponent n has been estimated (Fig. 6) by using plots of $\ln \ln [1/(1-\alpha)]$ *vs.* $\ln t$ as discussed by Sarkar and Ray [16]. In the present case,

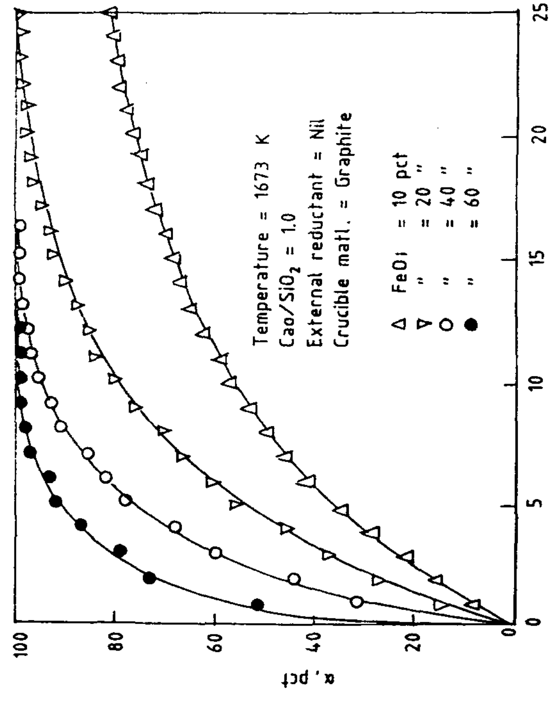

Fig. 4 Effect of initial FeO level in the slag on the rate of reduction

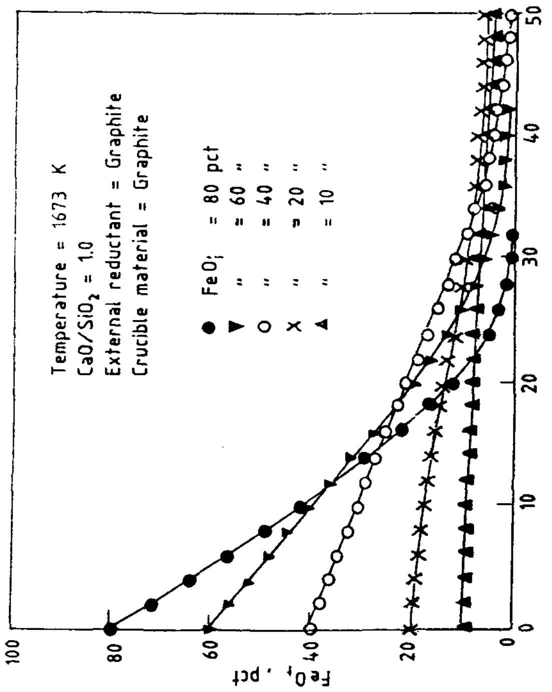

Fig. 5 Reduction of FeO rich slag by solid carbon

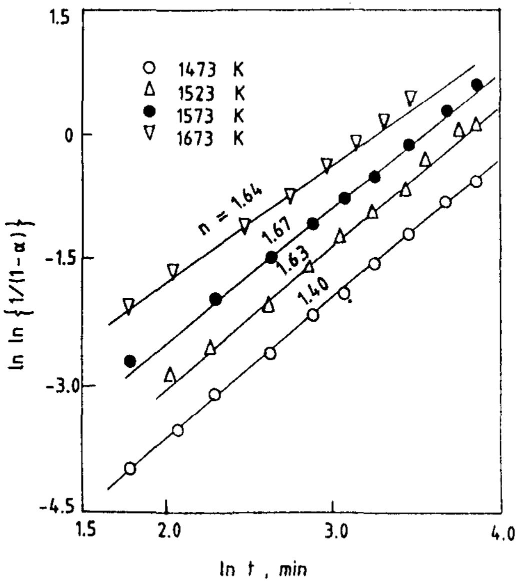

Fig. 6 Estimation of n values for the reduction reaction by solid carbon

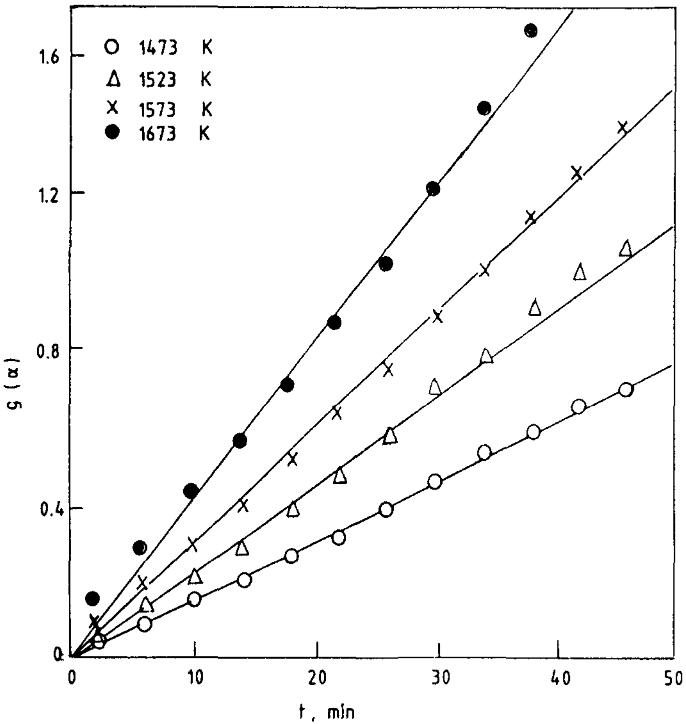

Fig. 7 Determination of rate constant at various temperatures

$n = 1.65$. The methods of analysing data according to J-M equation are given elsewhere [17]. However, it may be noted that the integral form of Eq. (5) is

$$[-\ln(1-\alpha)]^{1/1.65} = k't \tag{6}$$

where, k' is a constant.

Therefore, a plot of the L.H.S. of Eq. (6) *vs.* t is linear and the slope gives the rate constant value (Fig. 7).

The Arrhenius plot for the rate constant values is linear and the activation energy value is obtained as 108 kJ/mol which is in the range obtained by a differential approach (Fig. 8).

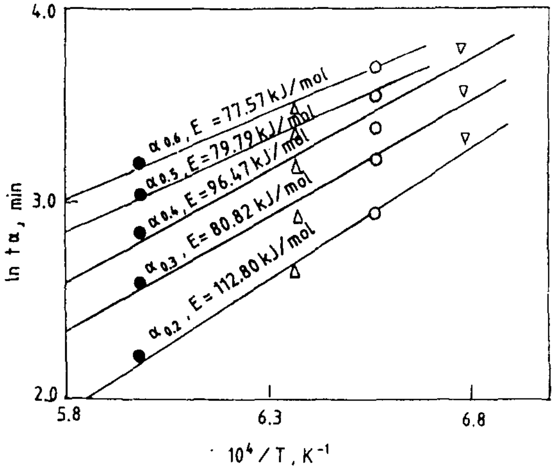

Fig. 8 Determination of activation energy values by differential approach

Conclusions

It is shown that reduction of iron oxide rich slags by a carbon saturated iron bath follows a first order kinetic equation. The reaction is retarded because of an induction delay when carbon source is the externally added graphite. In this case, the reaction kinetics is well described by the Johnson-Mehl equation:

$$\ln\left(\frac{1}{(1-\alpha)^{1.65}}\right) = k't \tag{7}$$

In either case the kinetics is improved by increase in temperature and initial FeO concentration. The rate also increases with CaO/SiO_2 level upto a value of 1.5.

References

1 I. D. Sommerville, P. Grieveson and J. Taylor, Ironmaking Steelmaking, 1 (1980) 25.
2 K. Upadhya, I. D. Sommerville and P. Grieveson, Ironmaking Steelmaking, 1 (1980) 33.
3 P. Grieveson and E. T. Turkdogan, Trans. Met. Soc. (AIME), 230 (1964) 1609.
4 F. Tsukihashi, K. Kato, K. Otsuka and T. Soma, Trans. ISIJ, 22 (1982) 688.
5 S. Ban-Ya, Y. Iguchi and T. Nagasaka, Trans. ISIJ, 23 (1983) B197.
6 T. Nagasaka, Y. Iguchi and S. Ban-Ya, Proc. Process Techn. Conf., Washington D.C., 1986. p. 669.
7 M. Sasabe and M. Uehara, Trans. ISIJ, 24 (1984) 34.
8 K. Kato, Y. Sasaki and T. Soma, Trans. ISIJ, 17 (1977) 532.
9 H. A. Fine, D. Meyer, D. Janke and H. J. Engell, Ironmaking Steelmaking, 12 (1985) 157.
10 G. Graenzdoerffer, W. M. Kim and H. A. Fine, Proc. Process Tech. Conf., 1988, 137.
11 W. M. Kim, G. Graenzdoerffer and H. A. Fine, Steel Research, 60 (1989) 166.
12 K. Koch, U. Harter and R. Bruckhaus, Steel Research, 60 (1989) 171.
13 K. Koch, U. Harter and R. Bruckhaus, Steel Research, 61 (1990) 14.
14 U. Harter and K. Koch, Steel Research, 61 (1990) 47.
15 U. Harter, R. Bruckhaus and K. Koch, Steel Research, 61 (1990) 53.
16 S. B. Sarkar and H. S. Ray, J. Thermal Anal., 36 (1990) 231.
17 P. Basu, On the Carbon Reduction of Iron Oxide Rich Slags, Ph. D. Thesis, IIT, Kharagpur, 1991.

Zusammenfassung — Vorliegend wird eine thermische Analyse der Reduktion von eisenoxidreichen Schlacken unter verschiedenen Bedingungen vorgestellt. Dabei wird der Einfluß bedeutender Verfahrensvariablen wie z.B. von Zeit, Temperatur, Kalk-Kieselerde-Verhältnis, FeO-Gehalt der Schlacke usw. diskutiert. Es wurde gezeigt, daß sich der Mechanismus der Reduktion bei Zusatz von Graphit von dem bei einem kohlenstoffgesättigten Bad unterscheidet, obwohl die Aktivierungsenergien ähnliche Werte aufweisen.