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GAMMA-RADIATION EFFECTS ON THE REDUCTION OF HEMATITE TO IRON IN THE GRAPHITE-IRON(III) OXIDE SYSTEM

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The effects of ^{60}Co-gamma radiation and of various sample composition on the reduction of hematite to iron in the graphite-iron(III) oxide system in air were studied using isothermal and dynamic TG techniques. Kinetic analysis of isothermal data were performed according to various theoretical models of heterogeneous reactions and the results showed that the three-dimensional phase boundary model gives the best fit of data. Analysis of dynamic TG data were made using Ozawa integral method, Coats-Redfern method and a composite method based on the modified Coats and redfern equation. The activation parameters were calculated and the results of the different methods were compared and discussed.

Radiation apparently did not introduce a change in the reaction model or mechanism. However, there is a decrease in activation energy and frequency factor upon irradiation and a decrease in the half-life time of the reaction which is remarkable at the higher temperatures and higher doses.

Keywords: gamma radiation effects, graphite-hematite system, kinetics

Introduction

The use of thermoanalytical methods to study the reduction of metal oxides has been used by several workers, Székely and Gaballah [1] developed dynamic method as a test procedure for assessing coke reactivity in the iron blast-furnace.

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Furuichi *et al.* [2] used TG to study the reduction of α-Fe_2O_3 prepared from iron salts at various temperatures and concluded that the oxides prepared at lower temperatures are more active for hydrogen. Sayama *et al.* [3] applied high pressure DTA flow method to study reactivity in the system H_2-hematite and investigated the effects of reduction conditions such as reaction temperature, H_2 pressure and H_2 flow rate. The results showed that the reduction rate is practically determined by the supply of the reactant, H_2 gas.

Different reactions, depending upon temperature, could occur in the graphite-iron(III) oxide system in a blast-furnace during the manufacture of cast iron [4, 5]. In many cases, the rate of reduction is controlled by heat transfer or by the rate at which material is supplied by flowing, since when the temperature is high enough the diffusional processes and the phase boundary reactions will no longer be rate determining. However, the reactivity in this system is determined by the gasification reaction of graphite.

High-energy radiation can be used to introduce changes into solids and that these defects may influence various manifestations of reactivity [6]. The influence of radiations on the chemical and catalytic reactivity of a solid has been studied only in few cases. Electron microscopic studies of the effects of radiation on graphite showed that irradiations lead to a pitting attack by oxygen over the entire surface [7]. In the present study, we made a detailed kinetic study of reactivity in the graphite-hematite system using isothermal and dynamic thermogravimetric techniques. The effects of ^{60}Co-gamma radiation on the kinetic and activation parameters of the reaction were also investigated.

Experimental

Iron(III) oxide, (Koch-Light Labs., Ltd., more than 99.995% pure), and pure graphite powder, (particle size less than 125 μm), were used in this study. The graphite and hematite powders were separately weighed and were thoroughly mixed in different ratios to get a homogeneous mixture of the specified composition.

The DTA-TG behaviour of the iron(III) oxide-graphite mixtures with different compositions were studied in air using Shimadzu Model 30 Thermal Analyzer. The kinetics of the gasification-reduction reaction were studied under 1 atm pressure in air flow (50 ml/min), in order to prevent the accumulation of gaseous products. In isothermal studies, the reaction temperatures changed between 645° and 725°C and in dynamic studies the temperature was raised up to 1000°C at heating rates of 5, 10, 15, 20 and 30 deg·min^{-1}. In all experiments, the sample weight in the Pt-cell of the thermal analyzer was kept at about 8 mg, in order to ensure linear heating rates and accurate temperature measurements.

For irradiation, samples were placed in glass-stoppered pyrex tubes and were irradiated in air using ^{60}Co-Gammacell 220 (Atomic Energy of Canada, Ltd., Commercial Products Div., Ottawa, Canada).

Samples were exposed to successively increasing doses at a dosimeter rate of $(1.2\pm0.04)10^5$ rad·h^{-1}.

Results and discussion

The kinetics and mechanisms of reactions in hematite-carbon powder mixtures have been studied in vacuum and in different gas atmospheres by several workers [4]. The results have shown that carbon monoxide is the essential reducing agent in the reduction of hematite to iron and that the kinetics of this system is determined by the gasification reaction of graphite. Hence, the reactivity in the graphite-hematite powdered mixtures could be followed by TG techniques and the results afford a measure for the reduction of hematite to iron. The results of the gasification-reduction experiments can be presented in the form of fractional reaction(α) *vs.* time(t) plots. The fractional reaction values were computed from the experimental weight loss data, relative to the values of the weight loss corresponding to complete reaction.

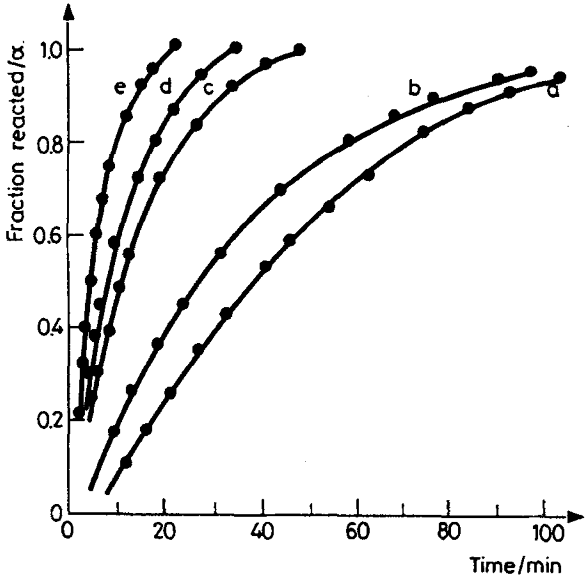

Fig. 1 Isothermal α-t curves for graphite-iron(III) oxide system in air (40.3 wt% graphite): (a) 649°; (b) 665°; (c) 683°; (d) 702° and (e) 724°C

Figure 1 shows typical α-t curves for the isothermal reactions in the graphite-iron(III) oxide system in air at a flow rate of 50 ml·min^{-1} for non-irradiated mixtures with 40.3 wt% graphite. Comparison of the fractional reaction-time curves with various theoretical expressions, derived for the appropriate nucleation and growth models could be used as evidence for the identification of the geometry of interface advance.

Under isothermal conditions, the rate constant k is independent of reaction time so that $kt = g(\alpha)$. The function $g(\alpha)$ depends on the mechanism controlling the reaction and on the size and shape of the reacting particles. The isothermal α-t data were analyzed according to the various kinetic models [8–11], given in Table 1, by the regression analysis. The results show that the three-dimensional phase boundary (R_3 model) and the first-order kinetics (F_1 model) gave the best fit of data under the present experimental conditions. The activation parameters were calculated based on these two models and the results are given in Table 2 in comparison with those obtained using non-isothermal methods.

Table 1 Kinetic equations* examined in this work

Reaction model	$g(\alpha)$	Function symbol
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$\alpha+(1-\alpha)\ln(1-\alpha)$	D_2
Jander equation, three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$	D_3
Ginstling-Brounshtein equation, three-dimensional diffusion	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	D_4
Two-dimensional phase boundary reaction	$[1-(1-\alpha)^{1/2}]$	R_2
Three-dimensional phase boundary reaction	$[1-(1-\alpha)^{1/3}]$	R_3
First-order kinetics	$[-\ln(1-\alpha)]$	F_1
Random nucleation: Avrami equation	$[-\ln(1-\alpha)]^{1/2}$	A_2
Random nucleation Erofeev equation	$[-\ln(1-\alpha)]^{1/3}$	A_3

*Refernces [8–11]

The kinetic behaviour of the gasification-reduction reaction was also investigated under non-isothermal conditions. Figure 2 shows the results obtained from dynamic measurements for samples with 40.3 wt% graphite in air at a flow rate of 50 ml·min^{-1}. In view of the conclusions from isothermal studies, only the F_1 and R_3 functions should be used to analyze the results. In the analysis of dynamic TG curves we assumed R_3 function and made a comparison of three integral dynamic methods, one due to Ozawa [12], the other is the Coats-Redfern method [13] and the third is a composite method based on Coats-Redfern modified equation [11].

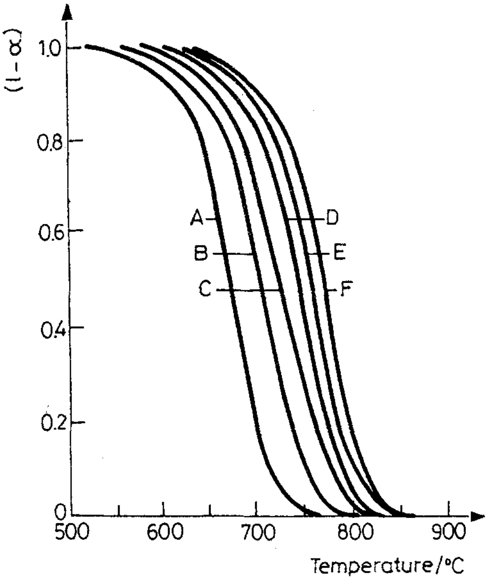

Fig. 2 Dynamic TG measurements for the graphite-iron(III) oxide system in air (40.3 wt% graphite). Heating rate: (A) 2.0; (B) 5.0; (C) 10.0; (D) 15.0; (E) 20.0 and (F) 30.0 deg·min^{-1}

In the Ozawa approximate integral method, a master curve could be derived from the thermogravimetric data obtained at different heating rates (β), and the activation energy could be calculated by LR analysis from logβ–(1/T) data at selected values of (1–α). The frequency value was calculated from the equation:

$$\log A = \log g(\alpha) - \log\left[\frac{E}{\beta R}P\left(\frac{E}{RT}\right)\right] \qquad (1)$$

where the function $P\left(\frac{E}{RT}\right)$ was approximated using the equation:

$$\log P\left(\frac{E}{RT}\right) = -2.315 - 0.4567\left(\frac{E}{RT}\right) \qquad (2)$$

The results, given in Table 2, show good agreement with the values obtained under isothermal conditions.

In the composite analysis of dynamic TG data, the results obtained, not only at different heating rates but also having different (1–α) values are superimposed on one master curve. In applying this method, use was made of Coats and redfern modified equation [9], which upon rearrangement could be written in the form:

$$\ln\left(\frac{\beta g(\alpha)}{T^2}\right) = \ln(AR/E) - (E/RT) \tag{3}$$

Therefore, the dependence of ln $(\beta g(\alpha)/T^2)$, calculated for the different α-values at the corresponding β-values, on $(1/T)$ should give rise to a single master straight line for the correct form of $g(\alpha)$, and hence a single activation energy and frequency factor could be readily calculated. Figure 3 shows the results obtained for the dynamic thermal behaviour of a sample having 40.3 wt% graphite. However, the values of E and ln A, given in Table 2, are not in agreement with the isothermal data of the Ozawa integral method. The discrepancies obtained in these treatments may be due to the simplifying assumption inherent in the use of the modified Coats-redfern equation and also to the possible inaccuracy of the R_3-model to describe the movement of the reaction interface over the whole range of reaction and at the different heating rates. Non-isothermal results are also subject to errors due to the effect of sample size and shape on heat flow. In general, isothermal results are more reliable and gave results which are in better agreement with those obtained by other workers [4, 14] using different experimental techniques.

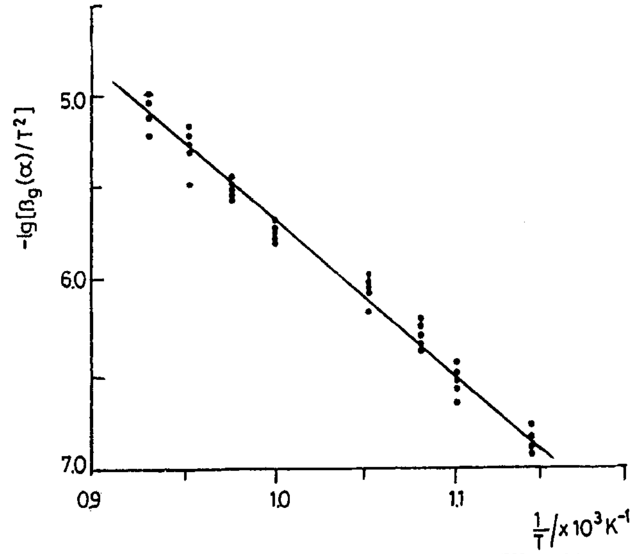

Fig. 3 Composite analysis of dynamic TG data for the graphite-iron(III) oxide system with 40.3 wt% graphite

Mixtures of graphite-iron(III) oxide powders having the composition 40.3 or 80.0 wt% graphite, were irradiated for different doses up to about 1.7 MGy. Isothermal studies of the irradiated samples were done in the temperature range 645°–680°C and the analysis of data according to the various kinetic models have shown that, the F_1- and R_3-models again gave the best fit to describe the reaction.

Table 2 Activation parameters for R3 model calculated according to isothermal and dynamic methods. Sample composition: 40.3 wt% graphite

Method	E /kJ·mol^{-1}	log A /min^{-1}
Isothermal	215±7	10.3±0.7
Dynamic		
(a)Ozawa [12]	205±13	9.5±0.6
(b) Coats-Redfern [9, 13]		
Heating rate: 2	178	7.9
5	169	7.4
10	160	6.0
15	167	6.4
20	193	7.8
30	211	7.3
Average:	180±19	7.1±0.7
(c) Composite method [11]	144±17	6.1±0.6

Table 3 Effect of gamma radiation on the kinetic parameters of the isothermal reaction in the graphite-iron(III) oxide system in air

Radiation dose / MGy	R_3-function		F_1-function	
	log A /min^{-1}	E /kJ·mol^{-1}	log A /min^{-1}	E /kJ·mol^{-1}
(a) Sample composition: 40.3 wt% graphite				
Non-irradiated	9.6	208.7	11.0	222.5
0.18	6.3	148.1	7.5	159.1
0.38	3.2	95.5	4.5	106.8
0.75	3.8	105.7	4.7	110.6
1.71	5.6	135.1	7.6	158.8
(b) Sample composition: 80.0 wt% graphite				
Non-irradiated	5.6	141.2	6.8	150.7
0.18	2.7	87.6	4.8	113.3
0.38	3.3	97.7	3.7	93.6
0.77	5.0	128.9	6.6	145.0
1.75	5.1	129.3	6.1	133.8

This indicates that radiation apparently did not introduce a change in the reaction model and mechanism. Table 3 summarizes the effects of radiation on the activation parameters of the isothermal reaction in graphite-iron(III) oxide system; these samples were irradiated for different doses and having a composition of 40.3 and 80.0 wt% graphite. The results showed irregular variations in activation parameters with dose but, there is a general decrease in activation energy and the frequency factor upon irradiation with a rate which is large at small doses. Table 4 shows the effect of radiation dose on the time for half-completion of the reaction ($t_{1/2}$). The results show a regular and remarkable decrease in $t_{1/2}$-values with increasing radiation dose, which is dependent upon reaction temperature and sample composition. This entirely represents the net effect on the frequency factor and the activation energy as well.

Table 4 Effect of gamma radiations on the $t_{1/2}$-values

Radiation dose / MGy	$t_{1/2}$ /min 646.5±1°C	666.5±1°C	685.5±1°C
(a) Sample composition: 40.3 wt% graphite			
Non-irradiated	37	27	10.5
0.18	30	19	13
0.38	30	20	14
0.75	22	18	13
1.71	19	13	9
(b) Sample composition: 80.0 wt% graphite			
Non-irradiated	54	33	20
0.18	45	30	23
0.38	40	25	21
0.77	36	22.5	16
1.75	23	15	11

In conclusion, radiation apparently did not introduce a change in reaction model or mechanism, but causes a decrease in activation energy and frequency factor which is remarkable at the higher reaction temperatures and higher radiation doses.

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Zusammenfassung — Mittels isothermer und dynamischer TG wurde im Graphit-Eisen(III)oxidsystem in Luft der Einfluß von ^{60}Co-Gammastrahlung und von verschiedenen Probenzusammensetzungen auf die Reduktion von Hämatit zu Eisen untersucht. Entsprechend verschiedener theoretischer Modelle heterogener Reaktionen wurde eine kinetische Analyse der isothermen Daten durchgeführt und die Ergebnisse zeigten, daß das dreidimensionale Phasengrenzenmodell die beste Übereinstimmung liefert. Die Analyse der dynamischen TG-Daten wurde mittels der Integralmethode von Ozawa, der Coats-Redfern-Methode und einer zusammengesetzten Methode auf der Grundlage der modifizierten Coats und Redfern Gleichung durchgeführt. Die Aktivierungsparameter wurden berechnet und die Ergebnisse der verschiedenen Methoden miteinander verglichen und diskutiert.

Strahlung scheint keine Änderung des Reaktionsmodelles oder des Mechanismus hervorzurufen. Durch Bestrahlung gibt es aber ein Absinken der Aktivierungsenergie und des Frequenzfaktors sowie ein Absinken der Halbwertszeit der Reaktion, was bei höheren Temperaturen und höherer Dosis bemerkenswert groß ist.