Thermochimica Acta, 56 (1982) 269–283
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

KINETICS OF DENSIFICATION OF POWDER COMPACTS DURING THE INITIAL STAGE OF SINTERING WITH CONSTANT RATES OF HEATING. A THERMAL ANALYSIS APPROACH.
PART. II. HAEMATITE COMPACTS

T.P. BAGCHI and P.K. SEN

Metallurgical Engineering Department Indian Institute of Technology, Kharagpur-721302 (India)

(Received 20 January 1982)

ABSTRACT

In Part I of this paper, a new technique for the analysis of densification kinetic data of powder compacts, obtained during sintering under constant heating rates, has been suggested.

In this part, the results of investigations on the densification characteristics of haematite compacts, sintered under linearly rising temperature, are presented. Small cylindrical compacts, prepared from haematite powder of varying particle sizes, were sintered in air inside a vertical tube-furnace in the temperature range 1173–1373 K. Continuous and in situ recording of linear shrinkage (ΔL) of the compacts was done by a mechanical-type dilatometer. From the recorded values of ΔL, the values of α at different temperatures (T) and times (t) were calculated.

These kinetic data (α vs. T) were then analysed according to various methods suggested in Part I. The most probable rate law governing the densification processes is seen to be the Ginstling–Brounshtein equation which indicates a three-dimensional diffusion-controlled mechanism.

The results (E and A) obtained for various sets of experiments conform excellently with the 'Kinetic Compensation Effect' which is usually observed in many non-isothermal processes.

INTRODUCTION

The present work was undertaken to study the process of densification of powder compacts while sintered under constant heating rates. In Part I of this paper, mathematical methods of analysing non-isothermal densification kinetic data have been proposed [1]. In this part, results of such analyses, as obtained by analysing the densification kinetic data of haematite powder compacts are presented.

TABLE I

Particle size, length (L_0), diameter (D_0), mass (M) and porosity (P) of the green compacts and their corresponding heating rate (β), onset temperature (T_0) and total time (t_f) of sintering

Compact no.	Particle size	L_0 (m)	D_0 (m)	M (kg)	P	β (K min^{-1})	T_0 (K)	t_f (s)
I/1	$-75\ \mu m, +63\ \mu m$	0.999×10^{-2}	0.1001×10^{-1}	0.25266×10^{-2}	0.3808	10	1133	1440
I/2		0.894×10^{-2}	0.1002×10^{-1}	0.21453×10^{-2}	0.4136	10	1103	1620
I/3		0.870×10^{-2}	0.1001×10^{-1}	0.20620×10^{-2}	0.4194	10	1133	1440
I/4		0.950×10^{-2}	0.1002×10^{-1}	0.22693×10^{-2}	0.4163	5	1133	3120
I/5		0.933×10^{-2}	0.1001×10^{-1}	0.21988×10^{-2}	0.4228	5	1103	3240
I/6		0.898×10^{-2}	0.1002×10^{-1}	0.21508×10^{-2}	0.4144	5	1103	3240
I/7		0.795×10^{-2}	0.1040×10^{-1}	0.20289×10^{-2}	0.4211	2	1113	7800
I/8		0.879×10^{-2}	0.1003×10^{-1}	0.20907×10^{-2}	0.4196	2	1113	7800
I/9		0.796×10^{-2}	0.1042×10^{-1}	0.19876×10^{-2}	0.4358	2	1113	7800
II/1	$-63\ \mu m, +53\ \mu m$	0.723×10^{-2}	0.1004×10^{-1}	0.17201×10^{-2}	0.4206	10	1103	1620
II/2		0.846×10^{-2}	0.1002×10^{-1}	0.20140×10^{-2}	0.3935	10	1113	1560
II/3		0.788×10^{-2}	0.1043×10^{-1}	0.20062×10^{-2}	0.4256	10	1113	1560
II/4		0.758×10^{-2}	0.1000×10^{-1}	0.17796×10^{-2}	0.4236	5	1093	3360
II/5		0.682×10^{-2}	0.1003×10^{-1}	0.16333×10^{-2}	0.4160	5	1103	3240
II/6		0.718×10^{-2}	0.1002×10^{-1}	0.17191×10^{-2}	0.4148	5	1103	3240

II/7		0.661×10^{-2}	0.1002×10^{-1}	0.15963×10^{-2}	0.4099	2	1093	8400
II/8		0.623×10^{-2}	0.1003×10^{-1}	0.14982×10^{-2}	0.4135	2	1093	8400
II/9		0.795×10^{-2}	0.1041×10^{-1}	0.19875×10^{-2}	0.4340	2	1093	8400
III/1	−53 μm, +45 μm	0.929×10^{-2}	0.1001×10^{-1}	0.21879×10^{-2}	0.4234	10	1243	780
III/2		0.970×10^{-2}	0.1000×10^{-1}	0.22500×10^{-2}	0.4307	10	1253	720
III/3		0.948×10^{-2}	0.1000×10^{-1}	0.21629×10^{-2}	0.4403	10	1263	660
III/4		0.957×10^{-2}	0.1000×10^{-1}	0.22120×10^{-2}	0.4330	5	1133	2880
III/5		0.850×10^{-2}	0.1003×10^{-1}	0.20985×10^{-2}	0.3983	5	1103	3240
III/6		0.874×10^{-2}	0.1003×10^{-1}	0.20415×10^{-2}	0.4299	5	1103	3240
III/7		0.757×10^{-2}	0.1041×10^{-1}	0.19001×10^{-2}	0.4318	2	1073	9000
III/8		0.945×10^{-2}	0.1001×10^{-1}	0.21959×10^{-2}	0.4305	2	1073	9000
III/9		0.775×10^{-2}	0.1039×10^{-1}	0.18996×10^{-2}	0.4430	2	1073	9000
IV/1	−45 μm, +38 μm	0.990×10^{-2}	0.1001×10^{-1}	0.22143×10^{-2}	0.3976	10	1263	660
IV/2		0.879×10^{-2}	0.1001×10^{-1}	0.21396×10^{-2}	0.4040	10	1263	660
IV/3		0.885×10^{-2}	0.1001×10^{-1}	0.21574×10^{-2}	0.4032	10	1263	660
IV/4		0.903×10^{-2}	0.1003×10^{-1}	0.22555×10^{-2}	0.3909	5	1233	1680
IV/5		0.824×10^{-2}	0.1001×10^{-1}	0.20341×10^{-2}	0.3956	5	1233	1680
IV/6		0.833×10^{-2}	0.1001×10^{-1}	0.20449×10^{-2}	0.3985	5	1233	1680
IV/7		0.916×10^{-2}	0.1001×10^{-1}	0.22571×10^{-2}	0.3968	2	1073	9000
IV/8		0.923×10^{-2}	0.1002×10^{-1}	0.22643×10^{-2}	0.4005	2	1143	6900
IV/9		0.770×10^{-2}	0.1039×10^{-1}	0.20435×10^{-2}	0.3970	2	1143	6900

EXPERIMENTAL

(i) Haematite powder

A typical Indian iron ore was selected for this study. It was crushed and sieved to four different particle size fractions, e.g. I(-75 μm, $+63$ μm), II(-63 μm, $+53$μm), III(-53 μm, $+45$ μm), IV(-45 μm, $+38$ μm). Chemical analyses showed that the variations in silica and alumina contents in different size-fractions were between 2.61–2.72% and 3.91–4.08%, respectively. Theoretical density (ρ_{th}) of the haematite powder is 5200 kg m^{-3} as determined by pyknometry.

(ii) Compaction

Small cylindrical compacts were prepared by pressing the powder from both ends in a die with a compaction pressure of 49.03 MPa. A suspension of zinc stearate in acetone was used as a lubricant for the die and punch.

(iii) Sintering

The compacts were sintered in a vertical tube furnace (heating elements, silicon carbide rods) in an ordinary atmosphere. Linear shrinkage behaviour of the compacts during sintering was noted with the help of a dilatometer (mechanical type). The dilatometer consists of one vertical quartz tube (closed at the bottom end) and one vertical quartz rod between which the compact is placed. The compact is located on the flat bottom of the tube, the quartz pusher rod rests upon the compact and acts as a link between the top surface of the compact and a dial gauge (whose least count is 0.0001 in. or 0.254×10^{-5} m). Any change in length of the compact is thus read in the dial gauge.

Thirty six compacts of haematite were heated under constant heating rates from room temperature (~ 298 K) to 1373 K. The initial dimensions, mass (M) and porosity (P) of the green compacts are given in Table 1. Rate of heating (β), onset temperature (T_0) (i.e. the temperature from which measurable shrinkage takes place), total time (t_f) of sintering, [here, $t_f = (1373 - T_0)/\beta$] for each compact are also shown in Table 1.

Since the objective of this investigation was to study the kinetics of early-stage densification, each compact was sintered up to a volume shrinkage ($\Delta V/V_0$) of 12% (approx.), which corresponds to $\alpha = 0.3$ (approx.). Subsequent SEM studies have not indicated initiation of grain growth phenomena within this extent of densification.

TABLE 2

Values of linear shrinkage (ΔL), densification parameter (α) and ($d\alpha/dT$) at different times and temperatures—compact No. I/1, particle size: (-75 μm, $+63$ μm), $\beta = 10$ K min^{-1}

Time (t) (s)	Temperature (T) (K)	Linear shrinkage (ΔL) (m)	Densification parameter (α)	$d\alpha/dT)$ (K^{-1})
0	1133	0.0	0,0	
60	1143	0.25400×10^{-5}	$0{,}22415900\times10^{-2}$	0.148100×10^{-4}
120	1153	0.50800×10^{-5}	$0{,}44238400\times10^{-2}$	0.712500×10^{-4}
180	1163	0.76200×10^{-5}	$0{,}66053000\times10^{-2}$	$0\ 129550\times10^{-3}$
240	1173	$0\ 11430\times10^{-4}$	$0{,}98744700\times10^{-2}$	0.189780×10^{-3}
300	1183	0.15240×10^{-4}	$0{,}13141540\times10^{-1}$	0.252010×10^{-3}
360	1193	0.19050×10^{-4}	$0{,}16405190\times10^{-1}$	$0\ 316320\times10^{-3}$
420	1203	0.22860×10^{-4}	$0{,}19666750\times10^{-1}$	0.382780×10^{-3}
480	1213	0.27940×10^{-4}	$0{,}24001050\times10^{-1}$	0.451480×10^{-3}
540	1223	0.30480×10^{-4}	$0{,}26181190\times10^{-1}$	0.522500×10^{-3}
600	1233	0.35560×10^{-4}	$0{,}30517590\times10^{-1}$	0.595910×10^{-3}
660	1243	0.40640×10^{-4}	$0{,}34850050\times10^{-1}$	0.671800×10^{-3}
720	1253	$0\ 50800\times10^{-4}$	$0{,}43499470\times10^{-1}$	0.750270×10^{-3}
780	1263	$0\ 60960\times10^{-4}$	$0{,}52130510\times10^{-1}$	$0\ 831400\times10^{-3}$
840	1273	0.71120×10^{-4}	$0{,}60741590\times10^{-1}$	0.915280×10^{-3}
900	1283	0.88900×10^{-4}	$0{,}75765430\times10^{-1}$	$0\ 100200\times10^{-2}$
960	1293	0.10160×10^{-3}	$0{,}86460590\times10^{-1}$	0.109167×10^{-2}
1020	1303	0.11430×10^{-3}	$0{,}97126010\times10^{-1}$	$0\ 118438\times10^{-2}$
1080	1313	$0\ 12700\times10^{-3}$	$0{,}10776180\times10^{0}$	0.128023×10^{-2}
1140	1323	0.13970×10^{-3}	$0{,}11836708\times10^{0}$	0.137931×10^{-2}
1200	1333	0.15240×10^{-3}	$0{,}12894326\times10^{0}$	$0\ 148176\times10^{-2}$
1260	1343	0.17018×10^{-3}	$0{,}14369982\times10^{0}$	0.158766×10^{-2}
1320	1353	$0\ 18796\times10^{-3}$	$0{,}15839779\times10^{0}$	0.169710×10^{-2}
1380	1363	0.21590×10^{-3}	$0{,}18137813\times10^{0}$	0.181026×10^{-2}
1440	1373	0.25146×10^{-3}	$0{,}21041906\times10^{0}$	0.192718×10^{-2}

RESULTS AND DISCUSSION

Linear shrinkages (ΔL) of the compacts during sintering at definite time intervals were noted and with the help of eqns. (1) and (2) from Part I [1] the corresponding values of α were calculated. For instance, the values of ΔL

TABLE 3

Results of analysis of densification kinetic data for 36 haematite compacts according to Ingraham's method

Compact No.	β (K min^{-1})	E (kJ mole^{-1})	Correlation coefficient	Variance
I/1	10	195.02	0.977	0.05413
I/2	10	183.05	0.920	0 24475
I/3	10	214 87	0 945	0.15104
I/4	5	182 71	0.966	0.08931
I/5	5	175.59	0 972	0.07467
I/6	5	191.75	0.962	0.10848
I/7	2	208.25	0.978	0 07309
I/8	2	199.42	0.977	0 07470
I/9	2	198.91	0.968	0.09962
II/1	10	211.01	0.973	0.10198
II/2	10	220.81	0.940	0 21634
II/3	10	213.65	0.970	0 10603
II/4	5	187.90	0.990	0 03424
II/5	5	222.32	0.993	0.02830
II/6	5	225.42	0.993	0 03067
II/7	2	167.97	0.956	0.11721
II/8	2	155.62	0 981	0 04260
II/9	2	154.74	0.981	0.04221
III/1	10	492.58	0.980	0.07861
III/2	10	473.99	0.963	0.08479
III/3	10	479.26	0.954	0.10948
III/4	5	248.61	0.966	0.13369
III/5	5	187.99	0 984	0 04755
III/6	5	170.19	0.962	0.09474
III/7	2	149 09	0.994	0.01682
III/8	2	145.83	0.994	0 01727
III/9	2	150.18	0.994	0.01556
IV/1	10	571 29	0.934	0.27665
IV/2	10	524.35	0 953	0.16073
IV/3	10	512 88	0.953	0.15641
IV/4	5	426.34	0.942	0.21760
IV/5	5	417.30	0.923	0.28359
IV/6	5	425.08	0.922	0.24785
IV/7	2	139.67	0.976	0.05214
IV/8	2	219.22	0.952	0.13667
IV/9	2	223.95	0.952	0.14160

and the corresponding values of α at definite time and temperature intervals, as obtained while sintering specimen no. I/1, are tabulated in Table 2.

In order to get the values of $(d\alpha/dT)$ at various temperatures, a six-order polynomial of this type

$$\alpha = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^4 + A_5T^5 + A_6T^6 \tag{1}$$

is fitted to these data (α vs. T) by a least-squares method (with correlation coefficient = 0.998) and the values of $(d\alpha/dT)$ at different temperatures (T) were calculated and are tabulated (Table 2). Similar procedures were employed to obtain the value of α and $(d\alpha/dT)$ at different temperatures for the other 35 compacts from the recorded values of ΔL. These data were then subjected to the mathematical analyses proposed in Part I [1].

(i) Method of Ingraham

According to this method, a plot of ln $(\beta\alpha/T^3)$ vs. $(1/T)$ is expected to give a straight line fit of the experimental data. The experimental data obtained were fitted to this linear relationship by a linear least-squares method. In each case, a reasonably good mathematical fit is obtained. From the slope of each of the straight lines, the value of the 'derived activation

TABLE 4

Results of analysis of densification kinetic data of compact No. I/1 by the Coats and Redfern method using 17 kinetic functions as given in Table 1 [1]
Particle size: (−75 μm, +63 μm), $\beta = 10$ K min^{-1}

Function no.	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
1	431.11	$0\ 1629 \times 10^{14}$	0.981	0.2141
2	434.67	0.1183×10^{14}	0.982	0.2067
3	436.89	$0\ 3273 \times 10^{13}$	0.982	0.2140
4	438.82	0.4025×10^{13}	0.983	0.2035
5	133.81	0.1788×10^{3}	0.980	0.0232
6	95.08	0.5708×10	0.977	0.0127
7	56.60	0.1790	0.971	0.0062
8	37.22	0.3490×10^{-1}	0.962	0.0040
9	208.00	0.5439×10^{3}	0.981	0 0524
10	209.13	0.4084×10^{5}	0.981	0.0510
11	205.19	0.8072×10^{5}	0.979	0.0538
12	92.28	0.4197×10^{1}	0.974	0.0140
13	54.59	0.1443	0.967	0.0067
14	35.84	0.3062×10^{-1}	0.957	0.0040
15	210.97	0.1491×10^{6}	0.982	0.0504
16	216.83	0.2790×10^{6}	0.984	0.0472
17	213.95	0.1022×10^{6}	0.983	0.0483

energy (E)' is calculated. The results are shown in Table 3 along with correlation coefficients and variances of least-squares fitting.

(ii) Method of Coats and Redfern

The data (α vs. T), as obtained for specimen no. I/1 (see Table 2), are fitted to the linear relationship proposed by Coats and Redfern (cf. eqn. (4) from Part I [1]) using all the seventeen known forms (cf. Table 1 of Part I [1]) of $g(\alpha)$. The results are shown in Table 4.

From these results, it becomes difficult to pin-point the exact form of $g(\alpha)$, because for each of the seventeen functional forms of $g(\alpha)$, very good mathematical fitting of experimental data to the equation is obtained. This problem was faced [2] earlier while re-analysing the non-isothermal thermal dehydroxylation data of $Mg(OH)_2$ as published elsewhere [3]. It was pointed out clearly that from the results obtained by analysing the non-isothermal kinetic data by the method of Coats and Redfern, a logical discrimination of the probable form of the governing rate law [i.e. $g(\alpha)$] is extremely difficult. In order to circumvent this problem, a combined integral and differential method of analysis of non-isothermal kinetic data has been suggested [2]. These data (see Table 2) were subjected to this method of analysis.

TABLE 5

Results of analysis of densification kinetic data of compact No I/1 by the integral method using 17 kinetic functions (as given in Table 1 [1]). Particle size: (-75 μm, $+63$ μm), $\beta = 10$ K min^{-1}

Function no.	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
1	307.18	0.1667×10^{8}	0.993	0.0412
2	310.67	0.1193×10^{8}	0.994	0.0390
3	312.96	0.3326×10^{7}	0.994	0.0406
4	314.85	0.4048×10^{7}	0.994	0.0379
5	9.96	0.5270×10^{-3}	0.350	0.0217
6	−28.64	0.2215×10^{-4}	0.660	0.0326
7	−67.24	0.9296×10^{-6}	0.866	0.0464
8	−86.50	0.1908×10^{-6}	0.900	0.0543
9	84.24	0.1108	0.983	0.0076
10	85.20	0.8130×10^{-1}	0.983	0.0080
11	81.39	0.1654	0.984	0.0069
12	−315.06	0.1648×10^{-4}	0.705	0.0309
13	−69.17	0.7643×10^{-6}	0.875	0.0450
14	−87.96	0.1647×10^{-6}	0.904	0.0532
15	87.13	0.2970	0.982	0.0086
16	93.03	0.5447	0.981	0.0106
17	90.06	0.2009	0.982	0.0095

(iii) Combined integral and differential method

These data (α vs. T) were analysed according to the integral method (see eqn. (5) from Part I [1]) and the results are shown in Table 5. It may be seen that reasonable values of E and A are obtained (along with a good correlation coefficient and variance) only for the first four functional forms of g(α), each of which is indicative of a diffusion-controlled reaction mechanism.

Similary, the same data were analysed according to the differential method (see eqn. (6) from Part I [1]), and the results obtained are shown in Table 6. Here also, it is seen that acceptable values of E and A are obtained only for the first four functional forms of g(α). Similar observations were made while analysing the non-isothermal densification data of the remaining 35 specimens. So, it may be concluded that the densification process (early stage) is a diffusion-controlled process. Amongst these four functional forms of g(α), the first (parabolic law) and the second [Valensi (Barrer) equation] one may be ruled out as they indicate one- and two-dimensional diffusion-controlled mechanisms, respectively, whereas, the densification process is clearly a three-dimensional diffusion-controlled process. Between the third (Ginstling–Brounshtein equation) and the fourth (Jander equation) function,

TABLE 6

Results of analysis of densification kinetic data of compact No. I/1, according to the differential method using 17 kinetic functions (as given in Table 1 [1]). Particle size: (−75 μm, +63 μm), $\beta = 10$ K min^{-1}

Function no.	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
1	343.91	0.4204×10^9	0.953	0.3676
2	349.28	0.3609×10^9	0.956	0.3568
3	351.21	0.9728×10^8	0.956	0.3521
4	354.79	0.1396×10^9	0.958	0.3456
5	89.30	0.5877	0.803	0.1348
6	−ve			
7	−ve			
8	−ve			
9	147.15	0.2971×10^2	0.887	0.1805
10	148.81	0.2337×10^2	0.890	0.1777
11	142.25	0.3646×10^2	0.876	0.1884
12	−ve			
13	−ve			
14	−ve			
15	152.04	0.9686×10^2	0.897	0.1731
16	161.96	0.2607×10^3	0.914	0.1592
17	157.01	0.1591×10^3	0.906	0.1658

both of which are valid for three-dimensional diffusion-controlled processes, it appears logical to take the third one as the governing rate law, because, in other solid state diffusion-controlled reactions, it is observed that the Jander equation is followed only at the initiation of the process, followed subsequently by the Ginstling–Brounshtein equation. Drawing the same analogy

TABLE 7

Results of analysis of densification kinetic data for 36 compacts (cf Table 1) according to the method of Coats and Redfern. The Ginstling–Brounshtein equation is used as governing kinetic law

Compact no	β (K min^{-1})	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
I/1	10	436.89	0.3273×10^{13}	0.982	0.2139
I/2	10	413.82	0.1258×10^{13}	0.937	0.9614
I/3	10	476.21	0.2141×10^{15}	0.957	0.5713
I/4	5	413.32	0.4236×10^{12}	0.974	0.3401
I/5	5	396.15	0.7038×10^{11}	0.980	0.2601
I/6	5	431.62	0.2249×10^{13}	0.970	0.4233
I/7	2	466.07	0.2674×10^{14}	0.983	0.2737
I/8	2	448.24	0.7011×10^{13}	0.982	0.2678
I/9	2	445.27	0.3262×10^{13}	0.975	0.3709
II/1	10	470.05	0.2324×10^{15}	0.979	0.3809
II/2	10	485.33	0.6068×10^{15}	0.955	0.7638
II/3	10	473.90	0.2647×10^{15}	0.978	0.3753
II/4	5	421.69	0.5179×10^{12}	0.991	0.1451
II/5	5	494.46	0.4442×10^{15}	0.994	0.1208
II/6	5	498.19	0.8499×10^{15}	0.994	0.1140
II/7	2	382.38	0.7468×10^{10}	0.966	0.4557
II/8	2	358.47	0.9982×10^{9}	0.986	0.1573
II/9	2	354.95	0.2587×10^{9}	0.985	0.1731
III/1	10	1035.19	0.2477×10^{36}	0.982	0.3257
III/2	10	1001.40	0.8505×10^{34}	0.967	0.3413
III/3	10	1010.69	0.1829×10^{35}	0.959	0.4430
III/4	5	544.99	0.6574×10^{17}	0.973	0.5115
III/5	5	421.86	0.9631×10^{12}	0.989	0.1543
III/6	5	389.33	0.6128×10^{11}	0.971	0.3739
III/7	2	349.99	0.5535×10^{9}	0.996	0.0455
III/8	2	337.92	0.1574×10^{9}	0.996	0.0508
III/9	2	345.70	0.2515×10^{9}	0.996	0.0468
IV/1	10	1194.03	0.3427×10^{42}	0.940	1.1196
IV/2	10	1094.01	0.3660×10^{38}	0.959	0.6245
IV/3	10	1071.78	0.5147×10^{37}	0.958	0.6140
IV/4	5	900.08	0.1071×10^{31}	0.948	0.8658
IV/5	5	886.39	0.7775×10^{30}	0.932	1.1403
IV/6	5	899.16	0.3013×10^{31}	0.931	0.9831
IV/7	2	323.43	0.1309×10^{8}	0.981	0.2091
IV/8	2	487.13	0.1518×10^{15}	0.963	0.5201
IV/9	2	491.66	0.1232×10^{15}	0.964	0.5159

in this case also, it may be concluded that the governing rate law for the process of non-isothermal densification is the Cinstling–Brounshtein equation, which, in mathematical form, is

$$g(\alpha) = \left(1 - \tfrac{2}{3}\alpha\right) - (1 - \alpha)^{2/3} \tag{3}$$

Taking eqn. (3) as the functional form of g(α), the results of analysing the

TABLE 3

Results of analysis of densification kinetic data for 36 compacts (cf. Table 1) according to the integral method. The Ginstling–Brounshtein equation is used as governing kinetic law

Compact No.	β (K min^{-1})	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
I/1	10	312.96	0.3326×10^{7}	0 993	0 0406
I/2	10	307.14	0.5371×10^{7}	0 935	0 5509
I/3	10	345.54	0.1154×10^{9}	0 967	0.2329
I/4	5	301.36	0.1186×10^{7}	0.987	0 0929
I/5	5	289.68	0.3189×10^{6}	0 991	0 0613
I/6	5	319.70	$0\ 6055\times10^{7}$	0 981	0 1464
I/7	2	354.12	$0\ 6682\times10^{8}$	0 987	0 1186
I/8	2	336.24	0.1810×10^{8}	0.991	0 0810
I/9	2	333.35	$0\ 8561\times10^{7}$	0.986	0 1208
II/1	10	363.46	0.8867×10^{9}	0.988	0.1280
II/2	10	367.64	0.9162×10^{9}	0.693	0.3601
II/3	10	361.82	$0\ 6445\times10^{9}$	0 988	0.1205
II/4	5	320 16	$0\ 3288\times10^{7}$	0 966	0 3236
II/5	5	387.91	0.1624×10^{10}	0 989	0.1394
II/6	5	391 63	0.3078×10^{10}	0.988	0 1524
II/7	2	280 85	0.5190×10^{5}	0 965	0.2553
II/8	2	256.90	$0\ 7381\times10^{4}$	0 991	0.0540
II/9	2	253.38	0.1927×10^{4}	0.983	0 0968
III/1	10	789.67	0.5000×10^{25}	0 979	0 2294
III/2	10	684 71	0.4667×10^{21}	0.968	0 1548
III/3	10	694 41	$0\ 1012\times10^{22}$	0 961	0.1969
III/4	5	421.11	0.5420×10^{11}	0.977	0.2670
III/5	5	315.31	0.4086×10^{7}	0.996	0.0327
III/6	5	282.78	0.2800×10^{6}	0.982	0 1227
III/7	2	253 43	$0\ 8663\times10^{4}$	0 996	0.0271
III/8	2	245.43	0.2537×10^{4}	0.991	0 0557
III/9	2	253.22	0.3960×10^{4}	0.991	0 0578
IV/1	10	904.77	0.1574×10^{30}	0.935	0 7024
IV/2	10	804.62	$0\ 1809\times10^{26}$	0 959	0.3377
IV/3	10	782 51	0.2629×10^{25}	0.958	0 3325
IV/4	5	672 27	0.1077×10^{21}	0 940	0.5842
IV/5	5	658.83	$0\ 8122\times10^{20}$	0 923	0.7206
IV/6	5	656.66	0.7598×10^{20}	0.923	0.5962
IV/7	2	230.94	0.2199×10^{3}	0.954	0.2719
IV/8	2	356.51	0.8044×10^{8}	0 973	0 1987
IV/9	2	361.15	0.6548×10^{8}	0.974	0.1988

non-isothermal densification data of all 36 specimens were calculated according to the previously mentioned methods and are shown in Table 7 (Coats and Redferns method), Table 8 (integral method) and Table 9 (differential method). In all of these cases, the calculated values of E and those and A are logically acceptable and the values of correlation coefficients and those of the variances are quite satisfactory.

TABLE 9

Results of analysis of densification kinetic data for 36 compacts (cf. Table 1) according to the differential method. The Ginstling–Brounshtein equation is used as governing kinetic law

Compact no.	β (K min^{-1})	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
I/1	10	351.21	0.9728×10^{8}	0.957	0.3521
I/2	10	224.70	0.2157×10^{4}	0.964	0.1555
I/3	10	287.05	0.4428×10^{6}	0.977	0.1091
I/4	5	284.97	0.2379×10^{6}	0.985	0.0935
I/5	5	283.78	0.1696×10^{6}	0.984	0.1062
I/6	5	314.71	0.3166×10^{7}	0.974	0.1928
I/7	2	364.55	0.1683×10^{9}	0.991	0.0557
I/8	2	273.61	0.5247×10^{5}	0.996	0.0221
I/9	2	272.45	0.1271×10^{6}	0.992	0.0475
II/1	10	292.13	0.1131×10^{7}	0.994	0.0421
II/2	10	331.20	0.2617×10^{8}	0.971	0.2296
II/3	10	300.98	0.2154×10^{7}	0.992	0.0563
II/4	5	428.51	0.7599×10^{11}	0.989	0.1020
II/5	5	467.24	0.2266×10^{13}	0.954	0.5421
II/6	5	424.11	0.6140×10^{11}	0.990	0.0970
II/7	2	342.83	0.1601×10^{8}	0.994	0.0342
II/8	2	324.94	0.3784×10^{7}	0.983	0.1001
II/9	2	339.19	0.5225×10^{7}	0.988	0.0709
III/1	10	635.50	0.4426×10^{19}	0.986	0.1030
III/2	10	463.80	0.9626×10^{12}	0.972	0.0621
III/3	10	456.92	0.5318×10^{12}	0.964	0.0771
III/4	5	340.93	0.2945×10^{8}	0.984	0.1154
III/5	5	293.46	0.5117×10^{6}	0.993	0.0456
III/6	5	267.94	0.6556×10^{5}	0.984	0.0931
III/7	2	272.34	0.4961×10^{5}	0.996	0.0293
III/8	2	310.85	0.1041×10^{7}	0.972	0.1930
III/9	2	293.61	0.1644×10^{6}	0.987	0.1064
IV/1	10	652.32	0.2072×10^{20}	0.954	0.2529
IV/2	10	635.72	0.4397×10^{19}	0.968	0.1659
IV/3	10	600.46	0.1977×10^{18}	0.968	0.1453
IV/4	5	436.11	0.5353×10^{11}	0.958	0.1655
IV/5	5	412.67	0.1419×10^{11}	0.938	0.2231
IV/6	5	383.47	0.1080×10^{10}	0.935	0.2022
IV/7	2	326.08	0.1531×10^{7}	0.986	0.0913
IV/8	2	308.31	0.8479×10^{6}	0.979	0.1142
IV/9	2	308.27	0.4465×10^{6}	0.979	0.1186

TABLE 10

Kinetic compensation effect: $\ln A = aE + b$. Results of linear least-squares fitting

Method of calculation (T_c)	Values of E and A are taken from	Slope (a)	Intercept (b)	Correlation coefficient	Variance	Mean Temperature (K)
Coats and Redfern	Table 7	0.08885	− 10 36775	0.999	0.7285	1353.6
Intergral	Table 8	0.08935	− 13 39970	0.999	0 6325	1346.1
Differential	Table 9	0.08741	− 12.75499	0 998	0 4317	1375.9

The concept of the so-called 'kinetic compensation effect', commonly observed [4,5] in many non-isothermal processes, is also seen to be valid here. It is claimed that for a particular process, the values of E bear a linear relationship with $\ln A$ as given below

$$\ln A = aE + b \qquad (4)$$

where a and b are constants.

The slope (a) of the straight line is related to the so-called 'mean temperature (T_c)' according to the following relationship

$$a = \frac{1}{RT_c} \qquad (5)$$

or

$$T_c = \frac{1}{Ra} \qquad (5a)$$

where R = universal gas constant.

The values of E and A, as shown in Table 7, follow just such a linear relationship, as obtained by a linear least-squares fitting. Similarly the values of E and A, as shown in Tables 8 and 9 are also seen to follow such a linear compensating relationship. The results of linear least-squares fitting are shown in Table 10. In each of the three cases, the value of T_c was calculated, and it is seen that the value of T_c falls within the experimental temperature range (1173–1373 K). So, the kinetic compensation effect holds good for the non-isothermal densification process and it is not affected by the variations in heating rates and particle sizes of the compacts.

CONCLUSIONS

The analysis of the non-isothermal kinetic data obtained for heamatite powder compacts indicates that though the value of the 'derived activation energy (E)' can be obtained by the method of Ingraham, no idea of the 'derived frequency factor (A)' and the controlling mechanism for the process can be obtained.

With the assumption of a three-dimensional diffusion-controlled mechanism, described by the Ginstling–Brounshtein equation (which appears to be logical), it is observed that the values of E and A vary considerably with variations in the particle size of the compact as also with variations in the heating rates. Further, it has been demonstrated clearly that even for the same operative mechanism, the values of E and A, as calculated by the proposed integral and differential methods, lie intermediate between those obtained by the other two methods of analysis (i.e. Coats and Redferns method and Ingraham's method). This clearly establishes the fact that for such heterogeneous systems, the values of E and A are not only influenced by operating variables (like heating rate, particle size of the compact) but are also affected by the method of analysis. It would, therefore, be erroneous to assign a particular magnitude of E and that of A to a particular mechanism of the process, a procedure practised by many. A similar observation has been made by Šesták [6] to the effect that a good mathematical fit should not be the only criterion for establishing a particular mechanism of a kinetic process. The physical picture of the process is also equally, if not more, important.

Perhaps the establishment of the kinetic compensation effect by the non-isothermal kinetic data is an indirect proof of the correctness of the methods of mathematical analysis employed to a set of non-isothermal kinetic data. In the present case, it has been amply demonstrated that the well-known method of Coats and Redfern and the combined integral and differential method proposed by the authors [2] apply equally well to the establishment of the kinetic compensation effect. This would confirm that, irrespective of variations in the heating rates and particle sizes of the compacts, the densification process is controlled by a three-dimensional diffusion process (the most probable rate law is given by the Ginstling–Brounshtein equation) in the early stages of non-isothermal sintering of heamatite powder compacts.

REFERENCES

1 T.P. Bagchi and P.K. Sen, Thermochim. Acta, 56 (1982) 261.
2 T.P. Bagchi and P.K. Sen, Thermochim. Acta, 51 (1981) 175.
3 P H Fong and D T.Y. Chen, Thermochim Acta, 18 (1977) 273
4 P.K. Gallagher and D.W. Johnson, Jr., Thermochim. Acta, 14 (1976) 255.
5 J. Zsakó, J. Therm. Anal., 9 (1976) 101.
6 J. Šesták, J. Therm Anal, 16 (1979) 503