Thermochimica Acta, 61 (1983) 73–86
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 III. COPPER POWDER COMPACTS

T.P. BAGCHI and P.K. SEN

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

(Received 23 June 1982)

ABSTRACT

In Part I of this paper, a new mathematical method of analysis of densification kinetic data of powder compacts (sintered at a constant heating rate) was suggested and the results of the application of that method in analysing the densification kinetic data of haematite powder compacts were published in Part II.

In this part, the results of analysis of densification kinetic data of some copper powder compacts are presented. From the results obtained, it becomes evident that no single known rate law is sufficient to describe the full course of the densification process. However, during the initial stage of densification, the process is seen to be diffusion-controlled. The Ginstling–Brounshtein equation is taken to be the most probable rate law which governs the initial period of the densification process; the values of the derived Arrhenius parameters (E and A) were calculated. The results, as calculated for various sets of experiments, conform nicely with the kinetic compensation effect.

INTRODUCTION

A new method of analysis of non-isothermal densification kinetic data of powder compacts, obtained during sintering under a linearly rising heating program, has been proposed [1] in Part I of this paper. This technique, which is based on the well-established mathematical methods of non-isothermal kinetic data analysis, was employed in analysing the non-isothermal densification kinetic data of haematite powder compacts and the results appear [2] in Part II of this paper. In this part, the results of analysis of non-isothermal densification kinetic data of copper compacts are presented.

TABLE 1

Particle size distribution of the Copper powder as determined by conventional sieve analysis

Particle size (μm)	Percentage
+177	0.1099
−177, +149	0.0520
−149, +105	0.1815
−105, +74	0.1851
−74, +63	0.4505
−63, +44	3.9092
−44	95.1125

EXPERIMENTAL

Copper powder

The copper powder selected for the present investigation was a typical commercially available powder (electrolytic) which contains particles of irregular shapes and sizes. The powder was heated at 673 K in a stream of hydrogen (for a period of 3600 s) in order to remove the oxide layers from the surfaces of the particles. Then the powder was subjected to conventional sieve analysis, the particle-size distribution of the copper powder is shown in Table 1. The average particle size of the powder was 3.8 μm (determined by Fisher sub-sieve analysis). The apparent density of the powder was 1150 kg m^{-3} and its theoretical density (ρ_{th}) was 8950 kg m^{-3}.

Compaction

The copper powder was pressed from both ends into small cylindrical compacts in a hardened steel die. The die and the punch were lubricated by swabbing them with a suspension of zinc stearate in acetone. It was intended that each compact should have a porosity level of 40–50% and the compaction pressure (78.53 MPa) required to achieve this level of porosity was fixed by repeated trials. After compaction, all compacts were preserved in a desiccator till they were taken out for sintering.

Sintering

The compacts were sintered in a wire-wound vertical tube furnace under a vacuum of ~ 1.33 Pa maintained with the help of a rotary pump in order to avoid or minimise surface oxidation of the compacts during heating. The electric power fed to the furnace was controlled through a variac in order to

TABLE 2

Length (L_0), diameter (D_0), mass (M) and porosity (P) of the green Copper compacts and their corresponding heating rates (β), temperature range and total time (t_f) of sintering

Compact no.	L_o (m)	D_0 (m)	M (kg)	P	β K min^{-1}	Temperature range of sintering (K)	Total time (t_f) of sintering (s)
Cu/1	0.574 E−02	0.1271 E−01	0.34523 E−02	0.4703	5	823–1123	3600
Cu/2	0.713 E−02	0.1271 E−01	0.43298 E−02	0.4652	5	823–1123	3600
Cu/3	0.617 E−02	0.1271 E−01	0.36967 E−02	0.4727	5	823–1123	3600
Cu/4	0.635 E−02	0.1271 E−01	0.38263 E−02	0.4694	5	823–1123	3600
Cu/5	0.682 E−02	0.1271 E−01	0.41021 E−02	0.4703	10	833–1133	1800
Cu/6	0.691 E−02	0.1271 E−01	0.40670 E−02	0.4817	10	833–1133	1800
Cu/7	0.682 E−02	0.1271 E−01	0.40528 E−02	0.4765	10	833–1133	1800
Cu/8	0.685 E−02	0.1271 E−01	0.40740 E−02	0.4762	10	833–1133	1800
Cu/9	0.767 E−02	0.1269 E−01	0.46216 E−02	0.4677	15	898–1273	1500
Cu/10	0.760 E−02	0.1269 E−01	0.45901 E−02	0.4664	15	898–1273	1500
Cu/11	0.645 E−02	0.1269 E−01	0.39079 E−02	0.4649	15	898–1273	1500
Cu/12	0.724 E−02	0.1269 E−01	0.43732 E−02	0.4666	15	898–1273	1500
Cu/13	0.714 E−02	0.1269 E−01	0.43191 E−02	0.4656	20	873–1273	1200
Cu/14	0.710 E−02	0.1269 E−01	0.42707 E−02	0.4686	20	873–1273	1200
Cu/15	0.700 E−02	0.1269 E−01	0.42088 E−02	0.4686	20	873–1273	1200
Cu/16	0.677 E−02	0.1269 E−01	0.40365 E−02	0.4732	20	873–1273	1200
Cu/17	0.713 E−02	0.1269 E−01	0.42461 E−02	0.4739	25	973–1273	720
Cu/18	0.670 E−02	0.1269 E−01	0.39207 E−02	0.4830	25	973–1273	720
Cu/19	0.676 E−02	0.1269 E−01	0.40455 E−02	0.4713	25	973–1273	720
Cu/20	0.600 E−02	0.1269 E−01	0.36386 E−02	0.4644	25	973–1273	720

TABLE 3

Values of L_f, D_f, V_f, $(\Delta V_f/V_0)$ and $(\Delta D_f/\Delta L_f)$ of 20 Copper compacts

Compact no.	β, (K min^{-1})	L_f (m)	D_f (m)	V_f (m^3)	$(\Delta V_f/V_0)$	$\Delta D_f/\Delta L_f)$
Cu/1	5	0.469 E−02	0.1097 E−03	0.443 E−06	0.3913	1.6571428
Cu/2	5	0.588 E−02	0.1107 E−03	0.566 E−06	0.3744	1.312
Cu/3	5	0.504 E−02	0.1095 E−03	0.475 E−06	0.3937	1.5575221
Cu/4	5	0.521 E−02	0.1100 E−03	0.495 E−06	0.3855	1.50
Cu/5	10	0.559 E−02	0.1107 E−03	0.538 E−06	0.3782	1.3333333
Cu/6	10	0.561 E−02	0.1130 E−03	0.563 E−06	0.3583	1.0846153
Cu/7	10	0.564 E−02	0.1113 E−03	0.549 E−06	0.3166	1.338983
Cu/8	10	0.561 E−02	0.1117 E−03	0.550 E−06	0.3674	1.2419354
Cu/9	15	0.658 E−02	0.1127 E−03	0.656 E−06	0.3233	1.3027522
Cu/10	15	0.654 E−02	0.1131 E−03	0.657 E−06	0.3165	1.302
Cu/11	15	0.545 E−02	0.1139 E−03	0.555 E−06	0.3198	1.30
Cu/12	15	0.619 E−02	0.1132 E−03	0.623 E−06	0.3199	1.3047619
Cu/13	20	0.594 E−02	0.1124 E−03	0.589 E−06	0.3477	1.2083333
Cu/14	20	0.593 E−02	0.1127 E−03	0.592 E−06	0.3408	1.2136752
Cu/15	20	0.584 E−02	0.1123 E−03	0.578 E−06	0.3263	1.2586206
Cu/16	20	0.566 E−02	0.1119 E−03	0.557 E−06	0.3499	1.3513513
Cu/17	25	0.601 E−02	0.1138 E−03	0.611 E−06	0.3221	1.1696428
Cu/18	25	0.560 E−02	0.1140 E−03	0.572 E−06	0.3245	1.1727272
Cu/19	25	0.560 E−02	0.1135 E−03	0.567 E−06	0.3373	1.1551724
Cu/20	25	0.501 E−02	0.1140 E−03	0.512 E−06	0.3257	1.2979797

TABLE 4

Values of dial gauge readings (DG) and densification parameters (α) at different times (t) and temperatures (T) (for a Copper compact)

Compact no. Cu/5, heating rate (β) = 10 K min^{-1}

Data point	t (s)	T (K)	DG	α
0	0	833	0	0
1	30	838	6.5	0.012489
2	60	843	15.5	0.029701
3	90	848	25.0	0.047767
4	120	853	55.0	0.104151
5	150	858	77.0	0.144852
6	180	863	100.5	0.187734
7	210	868	115.0	0.213883
8	240	873	138.0	0.254888
9	270	878	161.0	0.295306
10	300	883	180.0	0.328265
11	330	888	197.0	0.357420
12	360	893	204.0	0.369331
13	390	898	223.0	0.401406
14	420	903	244.0	0.436405
15	450	908	260.0	0.462755
16	480	913	275.0	0.488024
17	510	918	290.0	0.511434
18	540	923	295.0	0.519455
19	570	928	301.0	0.529047
20	600	933	312.5	0.547322
21	630	938	329.0	0.573308
22	660	943	337.0	0.585805
23	690	948	345.0	0.599010
24	720	953	354.0	0.612142
25	750	958	362.0	0.624433
26	780	963	369.0	0.635135
27	810	968	375.0	0.644265
28	840	973	381.0	0.653361
29	870	978	382.5	0.655630
30	900	983	386.0	0.660915
31	930	988	390.0	0.666936
32	960	993	392.0	0.670693
33	990	998	395.5	0.675190
34	1020	1003	407.5	0.693097
35	1050	1008	419.0	0.710857
36	1080	1013	431.5	0.728472
37	1110	1018	435.0	0.733582
38	1140	1023	440.0	0.740862
39	1170	1028	445.0	0.748118
40	1200	1033	450.0	0.755347
41	1230	1038	453.5	0.760393
42	1260	1043	457.0	0.765427

TABLE 4 (continued)

Data point	t (s)	T (K)	DG	α
43	1290	1048	459.0	0.768298
44	1320	1053	461.0	0.771165
45	1350	1058	463.0	0.774028
46	1380	1063	464.5	0.776173
47	1410	1068	467.0	0.779742
48	1440	1073	469.0	0.782593
49	1470	1078	472.0	0.786864
50	1500	1083	474.0	0.789705
51	1530	1088	475.5	0.791834
52	1560	1093	476.0	0.793252
53	1590	1098	477.5	0.794668
54	1620	1103	478.5	0.796084
55	1650	1108	479.5	0.797498
56	1680	1113	480.0	0.798207
57	1710	1118	481.0	0.799620
58	1740	1123	482.0	0.801032
59	1770	1128	483.0	0.802443
60	1800	1133	484.0	0.803853

maintain a constant rate of heating at the hot zone of the furnace where the compact was located during sintering. The linear contractions (ΔL) of the compact during sintering were noted [at definite time intervals] by a mechanical type dilatometer as described [2] in Part II of this paper.

The dimensions, porosity levels, rates of heating (β), temperature range of sintering (T_0 to T_f) and total time (t_f) of sintering of densification for the twenty green copper compacts are tabulated in Table 2.

RESULTS AND DISCUSSION

Final dimensions of the sintered compacts

After sintering, each sintered compact was furnace cooled under vacuum ($\sim$ 1.33 Pa). The length (L_f) and diameter (D_f) of each sintered compact were measured. The measured values of L_f and D_f and the calculated values of V_f, ($\Delta V_f/V_0$) and ($\Delta D_f/\Delta L_f$) (where $\Delta V_f = V_0 - V_f$, $\Delta D_f = D_0 - D_f$ and $\Delta L_f = L_0 - L_f$) are given in Table 3. The method of calculation was discussed in ref. 1.

TABLE 5

Results of analysis of non-isothermal densification kinetic data of a Copper compact according to the method of Coats and Redfern [eqn. (1)], using seventeen functional forms of g(α)

Compact no. Cu/5; heating rate (β) = 10 K min^{-1}, range of α = 0–0.803853.

Function no.	E (kJ mol^{-1})	A (Hz)	Linear correlation coefficient	Variance
1	98.68	0.1101 E+03	0.716	1.13736
2	109.55	0.2999 E+03	0.745	1.17915
3	114.00	0.1322 E+03	0.756	1.19247
4	123.08	0.5317 E+03	0.777	1.21595
5	35.11	0.8581 E−01	0.718	0.14246
6	22.30	0.2311 E−01	0.655	0.08141
7	9.49	−0.8291 E−03	0.479	0.03732
8	3.10	−0.2105 E−04	0.225	0.02218
9	41.29	0.1111 E+00	0.649	0.28794
10	50.15	0.2237 E+00	0.710	0.30274
11	53.49	0.2516 E+00	0.730	0.30796
12	12.60	−0.3046 E−02	0.456	0.07467
13	3.01	−0.1641 E−04	0.176	0.03424
14	−1.76	−0.2424 E−05	0.146	0.02043
15	86.98	0.1343 E+03	0.856	0.33632
16	73.01	0.7860 E+01	0.816	0.32714
17	60.71	0.2335 E+01	0.767	0.31595

Mathematical analysis of densification kinetic data

The non-isothermal sintering data were analysed according to the methods as suggested [1] and employed [2] earlier. The procedure and results of mathematical analyses of the experimental data obtained for one powder compact [Compact no. Cu/5, heating rate (β) = 10 K min^{-1}] are discussed below.

The values of the dial gauge readings (DG), recorded at different times (t) and temperatures (T) of sintering, and the calculated values of the densification parameter (α) are tabulated in Table 4. Attempts were than made to fit these data (by the linear least-squares method) to the equation of Coats and Redfern [eqn. (1)]. The generalized mathematical form of the equation of Coats and Redfern is given by

$$\ln[g(\alpha)/T^2] = (-E/RT) + \ln[(AR/\beta E)(1 - 2\,RT/E)] \qquad (1)$$

All seventeen known [1] functional forms of g(α) were used and the results appear in Table 5. Mathematical fitting is very poor in each case.

The same data were fitted (by the linear least-squares method) to the

TABLE 6

Results of analysis of non-isothermal densification kinetic data of a Copper compact according to the integral method [eqn. (2)] using seventeen functional forms of $g(\alpha)$

Compact no. Cu/5; heating rate $(\beta) = 10$ K min^{-1}; range of $\alpha = 0$–0.803853.

Function no.	E (kJ mole^{-1})	A (Hz)	Linear correlation coefficient	Variance
1	38.48	0.3922 E−01	0.502	0.53943
2	49.35	0.9807 E−01	0.588	0.56768
3	53.85	0.4206 E−01	0.618	0.57619
4	62.92	0.1584 E+00	0.671	0.59249
5	−25.07	0.5550 E−04	0.981	0.00301
6	−37.88	0.1199 E−04	0.989	0.00376
7	−50.68	0.2590 E−05	0.967	0.02172
8	−57.08	0.1204 E−05	0.956	0.03713
9	−18.90	0.6887 E−04	0.712	0.04270
10	−10.03	0.1273 E−03	0.452	0.04804
11	−6.70	0.1381 E−03	0.316	0.04977
12	−47.59	0.2886 E−05	0.990	0.00555
13	−56.16	0.1002 E−05	0.971	0.02445
14	−61.94	0.5908 E−06	0.960	0.03976
15	26.79	0.5290 E−01	0.766	0.06212
16	12.82	0.3528 E−02	0.509	0.05780
17	0.53	0.1189 E−02	0.026	0.05314

TABLE 7

Results of analysis of non-isothermal densification kinetic data of a Copper compact according to the method of Coats and Redfern [eqn. (5)], using seventeen functional forms of $g(\alpha)$

Compact no. Cu/5, heating rate $(\beta) = 10$ K min^{-1}, range of $\alpha = 0$–0.295306.

Function no.	E (kJ mole^{-1})	A (Hz)	Linear correlation coefficient	Variance
1	910.28	0.6461 E+52	0.953	0.51081
2	927.18	0.3704 E+53	0.954	0.50503
3	933.05	0.1919 E+53	0.955	0.50518
4	944.08	0.9445 E+53	0.957	0.50608
5	282.50	0.2820 E+15	0.949	0.06559
6	208.45	0.9644 E+10	0.947	0.03654
7	134.26	0.2901 E+06	0.944	0.01627
8	97.04	0.1450 E+04	0.940	0.00930
9	404.62	0.4654 E+22	0.943	0.14955
10	417.81	0.1587 E+23	0.947	0.14713
11	422.12	0.1981 E+23	0.948	0.14741
12	195.38	0.1399 E+10	0.939	0.03693
13	125.38	0.7670 E+05	0.934	0.01671
14	90.38	0.5281 E+03	0.930	0.00954
15	459.34	0.1330 E+26	0.957	0.14150
16	445.23	0.8561 E+24	0.954	0.14292
17	430.99	0.2164 E+24	0.950	0.14657

TABLE 8

Results of analysis of non-isothermal densification kinetic data of a Copper compact according to the integral method [eqn. (6)], using seventeen functional forms of $g(\alpha)$

Compact no. Cu/5; heating rate (β) = 10 K min^{-1}; range of α = 0–0.295306.

Function No.	E (kJ mole^{-1})	A (Hz)	Linear correlation coefficient	Variance
1	618.00	0.5475 E+32	0.948	0.26007
2	634.54	0.2932 E+33	0.951	0.25918
3	640.59	0.1548 E+33	0.952	0.25806
4	651.98	0.7916 E+33	0.954	0.25684
5	14.26	0.1320 E−01	0.411	0.00679
6	−60.02	0.5797 E−06	0.887	0.00696
7	−134.25	0.2564 E−10	0.947	0.01527
8	−171.34	0.1713 E−12	0.952	0.02249
9	136.28	0.1527 E+06	0.898	0.03139
10	149.30	0.4931 E+06	0.914	0.03103
11	153.69	0.6166 E+06	0.919	0.03098
12	−73.20	0.8773 E−07	0.926	0.00654
13	−143.05	0.7271 E−11	0.955	0.01480
14	−177.92	0.6667 E−13	0.956	0.02210
15	190.81	0.3760 E+09	0.948	0.02989
16	176.55	0.2441 E+08	0.938	0.03028
17	162.66	0.6686 E+07	0.927	0.03076

TABLE 9

Results of analysis of densification kinetic data for 20 Copper compacts according to the method of Coats and Redfern. The Ginstling–Brounshtein equation is used as the governing kinetic law

Compact no.	β (K min^{-1})	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
Cu/1	5	719.17	0.4596 E+40	0.924	0.56361
Cu/2	5	537.21	0.9017 E+28	0.818	1.60552
Cu/3	5	1066.74	0.7671 E+61	0.951	0.79025
Cu/4	5	490.20	0.1013 E+26	0.810	1.60621
Cu/5	10	933.05	0.1919 E+53	0.955	0.50518
Cu/6	10	651.45	0.6241 E+35	0.930	0.64028
Cu/7	10	653.21	0.1188 E+36	0.945	0.43694
Cu/8	10	851.94	0.1641 E+48	0.947	0.60934
Cu/9	15	1121.49	0.1753 E+60	0.978	0.25905
Cu/10	15	778.42	0.4678 E+40	0.925	0.57304
Cu/11	15	740.19	0.4533 E+38	0.923	0.47498
Cu/12	15	822.28	0.1670 E+43	0.932	0.51294
Cu/13	20	764.08	0.1751 E+41	0.916	0.68763
Cu/14	20	755.36	0.5172 E+40	0.917	0.65984
Cu/15	20	906.47	0.1189 E+48	0.977	0.49252
Cu/16	20	774.22	0.6749 E+41	0.911	0.75028
Cu/17	25	530.96	0.5004 E+23	0.928	0.53550
Cu/18	25	660.41	0.5714 E+30	0.912	0.70384
Cu/19	25	685.76	0.2370 E+32	0.925	0.48453
Cu/20	25	583.83	0.1974 E+26	0.940	0.52363

integral equation [1] whose mathematical form is

$$\ln[g(\alpha)] - \ln(T - T_0) = (-E/RT) + \ln(A/\beta) \qquad (2)$$

The results, tabulated in Table 6, indicate that mathematical fitting is very poor in each case.

Similar observations were made from the results obtained for the remaining 19 copper powder compacts. It may, therefore, be concluded that during this extent of densification ($\alpha \simeq 0.8$), no single known functional form of g(α) is suitable to describe the entire process of densification. It is almost certain that for a metallic powder compact, nucleation and grain-growth phenomena would start almost immediately after the bonding between the particles is established during the initial stage of densification. The densification parameter (α), chosen for the mathematical analysis in the present case, is concerned essentially with the annihilation of pores as indicated by continuous volume shrinkage. In many cases, decrease of pore volume may occur simultaneously with nucleation and grain growth and, therefore, any rate law incorporating the densification parameter (α), which is a function of volume shrinkage, will be totally unable to describe a process where the rate-controlling process is nucleation and grain-growth phenomena.

TABLE 10

Results of analysis of densification kinetic data for 20 Copper compacts according to the integral method. The Ginstling–Brounshtein equation is used as the governing kinetic law

Compact no.	β (K min^{-1})	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
Cu/1	5	434.79	0.9063 E+20	0.900	0.27639
Cu/2	5	324.20	0.6243 E+13	0.727	1.05162
Cu/3	5	782.01	0.9782 E+41	0.948	0.45148
Cu/4	5	289.56	0.4440 E+11	0.712	1.03966
Cu/5	10	640.59	0.1548 E+33	0.952	0.25806
Cu/6	10	418.78	0.3293 E+19	0.920	0.30598
Cu/7	10	404.25	0.6312 E+18	0.939	0.18506
Cu/8	10	583.67	0.4411 E+29	0.942	0.31262
Cu/9	15	740.18	0.2247 E+36	0.987	0.07939
Cu/10	15	463.58	0.5338 E+20	0.912	0.24367
Cu/11	15	406.39	0.4512 E+17	0.904	0.18057
Cu/12	15	488.06	0.1420 E+22	0.923	0.20863
Cu/13	20	470.83	0.1077 E+22	0.891	0.34671
Cu/14	20	461.79	0.3086 E+21	0.893	0.32881
Cu/15	20	693.35	0.2929 E+33	0.982	0.22755
Cu/16	20	480.81	0.4013 E+22	0.883	0.39330
Cu/17	25	317.64	0.4298 E+10	0.929	0.19072
Cu/18	25	400.69	0.1528 E+15	0.898	0.31201
Cu/19	25	386.33	0.5114 E+14	0.915	0.17934
Cu/20	25	370.68	0.1577 E+13	0.948	0.18437

TABLE 11

Results of analysis of densification kinetic data for 20 Copper compacts according to the differential method. The Ginstling–Brounshtein equation is used as the governing kinetic law

Compact no.	β (K min^{-1})	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
Cu/1	5	222.56	0.5707 E+09	0.843	0.12471
Cu/2	5				
Cu/3	5	458.50	0.9871 E+23	0.954	0.13499
Cu/4	5				
Cu/5	10	370.19	0.4376 E+18	0.951	0.08697
Cu/6	10	325.57	0.4821 E+15	0.950	0.11171
Cu/7	10				
Cu/8	10				
Cu/9	15	619.20	0.2071 E+31	0.985	0.06077
Cu/10	15	224.07	0.1252 E+09	0.821	0.13152
Cu/11	15	191.54	0.2380 E+07	0.775	0.11682
Cu/12	15	253.11	0.5604 E+10	0.861	0.10810
Cu/13	20				
Cu/14	20				
Cu/15	20	534.64	0.1859 E+26	0.981	0.14196
Cu/16	20				
Cu/17	25	196.52	0.2016 E+06	0.904	0.10331
Cu/18	25	230.52	0.1874 E+08	0.865	0.14453
Cu/19	25	232.87	0.3945 E+08	0.875	0.10047
Cu/20	25	245.60	0.4718 E+08	0.944	0.08851

N.B. Results obtained by analysing the sintering data of Compact no. Cu/2, Cu/4, Cu/7, Cu/8, Cu/13, Cu/14, and Cu/16 are not logically acceptable.

Repeated trials were then made to fit the kinetic data up to different values of densification parameter (α) by progressively decreasing this value. Subsequently, it was observed that reasonably good fit was obtained with experimental data which fall in the range of $\alpha = 0 - 0.3$

For Compact no. Cu/5, data point no. 9 corresponds to $\alpha = 0.295306$ (cf. Table 4). These nine values of α (data point no. 1–9) were fitted to the equation of Coats and Redfern by the linear least-squares method, and the results are tabulated in Table 7. It is observed from these results that for all seventeen functional forms of g(α), the experimental data may be fitted to the linear relationship of Coats and Redfern with a reasonably good degree of accuracy. However, it would be irrational to propose that any one of these seventeen kinetic functions is a valid governing rate law for the densification process.

In order to pin-point the exact functional form of g(α) which governs the process of densification, the integral method [3] was tried. The results obtained are shown in Table 8. From these results, it becomes evident that

TABLE 12

Results of analysis of densification kinetic data for 20 Copper compacts according to the method of Ingraham

Compact no.	β (K min^{-1})	E (kJ $mole^{-1}$)	Correlation coefficient	Variance
Cu/1	5	334.86	0.914	0.13824
Cu/2	5	247.47	0.795	0.39754
Cu/3	5	508.13	0.945	0.19743
Cu/4	5	224.06	0.785	0.39565
Cu/5	10	441.35	0.950	0.12579
Cu/6	10	302.56	0.919	0.16033
Cu/7	10	302.87	0.936	0.10910
Cu/8	10	400.83	0.940	0.15345
Cu/9	15	531.97	0.975	0.06452
Cu/10	15	362.88	0.915	0.14124
Cu/11	15	343.29	0.912	0.11639
Cu/12	15	384.34	0.923	0.12683
Cu/13	20	356.24	0.905	0.16929
Cu/14	20	352.03	0.906	0.16311
Cu/15	20	431.16	0.973	0.12694
Cu/16	20	361.39	0.900	0.18494
Cu/17	25	241.69	0.914	0.13467
Cu/18	25	304.91	0.900	0.17540
Cu/19	25	315.98	0.913	0.12127
Cu/20	25	268.29	0.929	0.13332

reasonable values of the Arrhenius parameters (E and A) are obtained (along with good correlation coefficients and low variance) only for the first four functional forms of $g(\alpha)$, each of which is indicative of a diffusion-controlled reaction mechanism.

Following arguments similar to those expressed in ref. 2, the Ginstling–Brounshtein equation was taken as the governing rate law. Mathematical forms of the Ginstling–Brounshtein equation are

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

and

$$f(\alpha) = \tfrac{3}{2}\left[(1 - \alpha)^{-1/3} - 1\right]^{-1} \tag{4}$$

Using these functional forms of $g(\alpha)$ and $f(\alpha)$, the equation of Coats and Redfern, the integral equation and the differential equation would respectively assume the mathematical forms

$$\begin{aligned} \ln\left[\left\{\left(1 - \tfrac{2}{3}\alpha\right) - (1 - \alpha)^{2/3}\right\}/T^2\right] &= (-E/RT) \\ &\quad + \ln[(AR/\beta E)(1 - 2RT/E)] \end{aligned} \tag{5}$$

$$\ln\left[\left(1-\tfrac{2}{3}\alpha\right)-(1-\alpha)^{2/3}\right]-\ln(T-T_0)=(-E/RT)+\ln(A/\beta) \qquad (6)$$

and

$$\ln\left[\frac{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\cdot\frac{2}{3}\{((1-\alpha)^{-1/3}-1\}}{\frac{E(T-T_0)}{RT^2}+1}\right]=(-E/RT)+\ln(A/\beta) \qquad (7)$$

The sintering data were fitted to these three expressions by the linear least-squares method. The values of $(\mathrm{d}\alpha/\mathrm{d}T)$ were calculated by fitting a six-degree polynomial to each set of data. The values of the derived Arrhenius parameters are tabulated in Tables 9–11.

The values of E were also calculated by the method of Ingraham [4], which in mathematical form is

$$\ln[\beta\alpha/T^3]=(-E/RT)+\ln k_1 \qquad (8)$$

The experimental data (up to $\alpha \simeq 0.3$) were fitted to eqn. (8) by the linear least-squares method and the results obtained are tabulated in Table 12.

Kinetic compensation effect

The concept of the so-called kinetic compensation effect is seen to be valid here. It is claimed that for a particular process, the value of E bears a linear relationship with $\ln A$, viz.

$$\ln A = aE + b \qquad (9)$$

where a and b are constants.

However, since the physical significance of E and A is not clearly understood, the kinetic compensation effect is nothing more than an apparent effect. Garn [5,6] defined a "characteristic temperature (T_c)" which is related to the slope (a) of the straight line plot according to

TABLE 13

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

Method of Calculation	Values of E and A are taken from	Slope (a)	Intercept (b)	Correlation coefficient	Variance	Mean temperature T_c (K)
Coats and Redfern	Table 5	0.1433	−18.0081	0.978	0.16687	839.40
Integral	Table 6	0.1414	−19.2702	0.988	0.20876	850.36
Differential	Table 7	0.1356	−12.4145	0.993	0.32422	886.68

$$T_c = \frac{1}{Ra} \tag{10}$$

The physical significance of T_c is, however, not very clear.

The values of E and A, as calculated by the different methods [cf. Tables 9–11], were fitted to eqn. (9) by the linear least-squares method and the results are tabulated in Table 13. 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 (823–1273 K). So, the kinetic compensation effect holds good for the non-isothermal densification process of copper powder compacts and it is not affected by the variations in heating rates.

CONCLUSIONS

From the results obtained in the present investigation, it becomes evident that it is impossible to describe the entire process of densification of powder compacts with a single known kinetic law. However, the initial stage of densification (up to $\alpha = 0.3$) may be described by a three-dimensional diffusion controlled process (the Ginstling–Brounshtein equation is the most likely) where grain-growth phenomena and other structural changes are not predominant.

The values of the derived Arrhenius parameters (i.e. E and A) are dependent upon the method of calculation. Even using the same method of calculation, the values of these derived Arrhenius parameters depend upon the rates of heating. Hence, as pointed out earlier [2], it would be futile to predict the mechanism of the process by only considering the values of the derived Arrhenius parameters. As the theoretical significance of these parameters is not well-defined (at least, for non-isothermal heterogeneous processes), these parameters have only limited validity. Establishment of the kinetic compensation effect is, perhaps, an indirect proof of the validity of the present mathematical approach.

REFERENCES

1 T.P. Bagchi and P.K. Sen, Thermochim. Acta, 56 (1982) 261.
2 T.P. Bagchi and P.K. Sen, Thermochim. Acta, 56 (1982) 269.
3 T.P. Bagchi and P.K. Sen, Thermochim. Acta, 51 (1981) 175.
4 T.R. Ingraham, in H.G. McAdie (Ed.), Proc. 2nd Toronto Symp. Therm. Anal., Toronto, 1967, p. 21.
5 P.D. Garn, J. Therm. Anal., 7 (1975) 475.
6 P.D. Garn, J. Therm. Anal., 10 (1976) 99.