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

PART IV. SILVER POWDER COMPACTS

T.P. BAGCHI and P.K. SEN

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

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ABSTRACT

A new mathematical approach to the analysis of the non-isothermal densification kinetic data of various powder compacts (sintered under linearly increasing temperature) was suggested in Part I of this paper and that method was applied to the analysis of the densification data of haematite and copper powder compacts (vide Parts II and III of this paper, respectively). The same method was employed to analyse the densification kinetic data of some silver powder compacts and the results obtained are presented in this part of the paper.

The results indicate, once again, that no single known rate law is valid for the entire range of the densification process. However, the initial period is seen to be diffusion-controlled. The Ginstling–Brounshtein equation is chosen to be the probable rate law (as previously) and the values of the derived Arrhenius parameters (E and A) were calculated. The results conform with the kinetic compensation effect in this case also.

INTRODUCTION

The present series of investigations was undertaken to study the densification behaviour of different powder compacts during sintering under non-isothermal conditions. The results obtained have already been published in Part II (for haematite powder compacts) and Part III (for copper powder compacts) of this paper [1,2]. The non-isothermal sintering data were analysed by a new mathematical method [3]. In this part, the results of analysis of non-isothermal densification kinetic data of silver powder compacts are presented.

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TABLE 1

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

Particle size (μm)	Percentage
+88	
−88, +74	26.14
−74, +63	29.63
−63, +53	19.78
−53, +45	13.02
−45, +38	11.43
−38	

EXPERIMENTAL

Silver powder

A typical commercial silver powder (electrolytic grade), which contains particles of irregular shapes and sizes, was selected for the present experiment. Particle size distribution of the silver powder, as obtained by conventional sieve analysis, is given in Table 1.

Compaction

Small cylindrical compacts were made by pressing (from both ends) the silver powder in a hardened steel die. The compaction pressure (62.88 MPa) was adjusted so that each green compact contained 40–50% porosity. The 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 vacuum ($\sim$ 1.33 Pa) maintained with the help of a rotary pump. The details of the experimental set-up are given elsewhere [1,2]. The linear contractions (ΔL) of a compact during sintering were recorded by a dilatometer.

The dimensions, mass and porosity of each green compact are given in Table 2 which also includes rates of heating (β), temperature range of densification (T_0 and T_f) and total time (t_f) of densification.

After sintering, each compact was furnace cooled under vacuum ($\sim$ 1.33 Pa). The length (L_f) and diameter (D_f) of each sintered compact were measured and are tabulated in Table 3. Calculated values of V_f, ($\Delta V_f/V_0$) and ($\Delta D_f/\Delta L_f$) are also given in Table 3.

TABLE 2

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

Compact no.	L_0 (m)	D_0 (m)	M (kg)	P	β (K min^{-1})	Temperature range of sintering (K)	Total time (t_f) of sintering (s)
Ag/1	1.061×10^{-2}	1.271×10^{-2}	9.0884×10^{-3}	0.3570	5	873–1173	3600
Ag/2	1.046×10^{-2}	1.271×10^{-2}	8.9589×10^{-3}	0.3571	5	873–1173	3600
Ag/3	1.025×10^{-2}	1.2705×10^{-2}	8.3500×10^{-3}	0.3880	5	873–1173	3600
Ag/4	0.999×10^{-2}	1.2705×10^{-2}	8.1793×10^{-3}	0.3849	5	873–1173	3600
Ag/5	1.075×10^{-2}	1.271×10^{-2}	9.2989×10^{-3}	0.3507	10	873–1173	1800
Ag/6	1.043×10^{-2}	1.271×10^{-2}	9.0082×10^{-3}	0.3517	10	873–1173	1800
Ag/7	0.966×10^{-2}	1.2705×10^{-2}	7.9944×10^{-3}	0.3783	10	873–1173	1800
Ag/8	1.028×10^{-2}	1.2705×10^{-2}	8.7672×10^{-3}	0.3593	10	873–1173	1800
Ag/9	1.002×10^{-2}	1.2705×10^{-2}	8.1541×10^{-3}	0.3887	15	873–1173	1200
Ag/10	1.039×10^{-2}	1.2705×10^{-2}	8.5073×10^{-3}	0.3849	15	873–1173	1200
Ag/11	0.992×10^{-2}	1.2705×10^{-2}	8.0959×10^{-3}	0.3869	15	873–1173	1200
Ag/12	1.011×10^{-2}	1.2705×10^{-2}	8.2524×10^{-3}	0.3868	15	873–1173	1200
Ag/13	1.010×10^{-2}	1.2705×10^{-2}	8.3655×10^{-3}	0.3778	20	873–1173	900
Ag/14	1.004×10^{-2}	1.2705×10^{-2}	8.3177×10^{-3}	0.3776	20	873–1173	900
Ag/15	0.965×10^{-2}	1.2705×10^{-2}	7.9760×10^{-3}	0.3791	20	873–1173	900
Ag/16	0.965×10^{-2}	1.2705×10^{-2}	8.2197×10^{-3}	0.3782	20	873–1173	900
Ag/17	0.982×10^{-2}	1.2705×10^{-2}	8.0739×10^{-3}	0.3823	25	923–1173	600
Ag/18	0.997×10^{-2}	1.2705×10^{-2}	8.1008×10^{-3}	0.3896	25	923–1173	600
Ag/19	1.012×10^{-2}	1.2705×10^{-2}	8.1817×10^{-3}	0.3927	25	923–1173	600
Ag/20	1.007×10^{-2}	1.2705×10^{-2}	8.1764×10^{-3}	0.3900	25	923–1173	600

TABLE 3

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

Compact no.	β (K min^{-1})	L_f (m)	D_f (m)	V_f (m^3)	$(\Delta V_f/V_0)$	$(\Delta D_f/\Delta L_f)$
Ag/1	5	0.995×10^{-2}	1.150×10^{-2}	1.033×10^{-6}	0.2323	1.8333333
Ag/2	5	0.975×10^{-2}	1.142×10^{-2}	0.999×10^{-6}	0.2475	1.8169014
Ag/3	5	0.952×10^{-2}	1.140×10^{-2}	0.972×10^{-6}	0.2522	1.7876712
Ag/4	5	0.929×10^{-2}	1.143×10^{-2}	0.954×10^{-6}	0.2467	1.8142857
Ag/5	10	1.000×10^{-2}	1.140×10^{-2}	1.021×10^{-6}	0.2516	1.7466666
Ag/6	10	0.969×10^{-2}	1.140×10^{-2}	0.989×10^{-6}	0.2525	1.7702702
Ag/7	10	0.890×10^{-2}	1.132×10^{-2}	0.896×10^{-6}	0.2684	1.8223684
Ag/8	10	0.953×10^{-2}	1.137×10^{-2}	0.968×10^{-6}	0.2576	1.78
Ag/9	15	0.927×10^{-2}	1.137×10^{-2}	0.941×10^{-6}	0.2591	1.78
Ag/10	15	0.962×10^{-2}	1.139×10^{-2}	0.980×10^{-6}	0.2558	1.7077922
Ag/11	15	0.915×10^{-2}	1.139×10^{-2}	0.932×10^{-6}	0.2587	1.7077922
Ag/12	15	0.935×10^{-2}	1.138×10^{-2}	0.951×10^{-6}	0.2580	1.743421
Ag/13	20	0.935×10^{-2}	1.132×10^{-2}	0.941×10^{-6}	0.2651	1.847
Ag/14	20	0.932×10^{-2}	1.141×10^{-2}	0.953×10^{-6}	0.2513	1.7986111
Ag/15	20	0.892×10^{-2}	1.139×10^{-2}	0.909×10^{-6}	0.2570	1.8013698
Ag/16	20	0.920×10^{-2}	1.137×10^{-2}	0.934×10^{-6}	0.2581	1.8287671
Ag/17	25	0.920×10^{-2}	1.158×10^{-2}	0.969×10^{-6}	0.2216	1.8145161
Ag/18	25	0.937×10^{-2}	1.161×10^{-2}	0.992×10^{-6}	0.2152	1.825
Ag/19	25	0.951×10^{-2}	1.160×10^{-2}	1.005×10^{-6}	0.2166	1.8114754
Ag/20	25	0.950×10^{-2}	1.161×10^{-2}	1.006×10^{-6}	0.2122	1.9210526

TABLE 4

Results of analysis of densification kinetic data for 20 silver compacts according to the method of Coats and Redfern. The Ginstling–Brounshtein equation is used as governing rate equation [g(α)]

Compact no.	β (K min^{-1})	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
Ag/1	5	364.55	0.1715 E+16	0.932	0.45013
Ag/2	5	393.97	0.5401 E+17	0.914	0.77067
Ag/3	5	328.90	0.5634 E+13	0.924	0.66295
Ag/4	5	346.00	0.1351 E+15	0.938	0.39982
Ag/5	10	450.26	0.2152 E+21	0.969	0.26013
Ag/6	10	376.21	0.2089 E+17	0.942	0.37719
Ag/7	10	358.12	0.1394 E+16	0.959	0.24970
Ag/8	10	364.08	0.2993 E+16	0.956	0.28495
Ag/9	15	367.97	0.6725 E+16	0.949	0.35708
Ag/10	15	311.55	0.1781 E+13	0.942	0.44465
Ag/11	15	391.00	0.8022 E+17	0.933	0.62836
Ag/12	15	392.36	0.9456 E+17	0.934	0.62570
Ag/13	20	314.54	0.6018 E+13	0.937	0.40961
Ag/14	20	309.65	0.2102 E+13	0.943	0.42270
Ag/15	20	330.80	0.4637 E+14	0.947	0.37435
Ag/16	20	304.05	0.1414 E+13	0.940	0.38805
Ag/17	25	391.87	0.1602 E+17	0.948	0.35950
Ag/18	25	307.38	0.2257 E+12	0.932	0.44567
Ag/19	25	410.84	0.3535 E+17	0.955	0.49730
Ag/20	25	347.11	0.2384 E+14	0.955	0.35476

RESULTS AND DISCUSSION

All compacts were sintered up to $\alpha = 0.6$–0.7 and the densification kinetic data were analysed by the mathematical method suggested earlier [3]. It was observed from the results of such mathematical analyses that

(i) no single known functional form of g(α), as given elsewhere [3], is sufficient to describe the entire range of densification data;

(ii) the initial state (i.e. $\alpha \simeq 0.3$) of densification follows a mechanism which is governed by a diffusion-controlled process (the Ginstling–Brounshtein equation seems to be the most suitable rate equation in this case).

Similar conclusions were drawn on analysis of the non-isothermal densification kinetic data (initial stage) of haematite powder compacts [1] and copper powder compacts [2]. It may, therefore, be concluded that the initial stage of the densification process of silver powder compacts is governed by a three-dimensional diffusion-controlled process or, more specifically, by the

TABLE 5

Results of analysis of densification kinetic data for 20 Silver compacts according to the integral method. The Ginstling–Brounshtein equation is used as governing rate equation [g(α)]

Compact no.	β (K min^{-1})	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
Ag/1	5	208.11	0.2007 E+05	0.950	0.10429
Ag/2	5	246.12	0.1816 E+07	0.919	0.27863
Ag/3	5	205.34	0.5425 E+04	0.937	0.20228
Ag/4	5	195.57	0.3664 E+04	0.958	0.08154
Ag/5	10	288.58	0.9843 E+09	0.984	0.05658
Ag/6	10	220.76	0.2585 E+06	0.951	0.11000
Ag/7	10	208.38	0.3842 E+05	0.977	0.04669
Ag/8	10	214.41	0.8195 E+05	0.972	0.06138
Ag/9	15	219.31	0.2123 E+06	0.966	0.07969
Ag/10	15	191.79	0.2906 E+04	0.960	0.11325
Ag/11	15	253.48	0.1033 E+08	0.943	0.22099
Ag/12	15	254.77	0.1205 E+08	0.944	0.22068
Ag/13	20	183.90	0.2310 E+04	0.947	0.11581
Ag/14	20	190.37	0.3605 E+04	0.957	0.11741
Ag/15	20	200.29	0.1724 E+05	0.962	0.09636
Ag/16	20	177.42	0.9476 E+03	0.952	0.10300
Ag/17	25	233.28	0.4207 E+06	0.965	0.08495
Ag/18	25	178.36	0.2917 E+03	0.945	0.11827
Ag/19	25	281.78	0.3452 E+08	0.971	0.14568
Ag/20	25	218.00	0.2716 E+05	0.974	0.07773

Ginstling–Brounshtein equation whose mathematical forms are

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

and

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

Taking eqn. (1) as the valid functional form of g(α), the kinetic data were analysed by the well-known method of Coats and Redfern [3] and by the integral method of Bagchi and Sen [3]. The results of linear least-squares fittings are tabulated in Tables 4 and 5, respectively. Likewise, these data were analysed by the proposed differential method [3] [taking eqn. (2) as the valid functional form of f(α)] and the results are tabulated in Table 6. These data were also analysed by the method of Ingraham [3] and the calculated values of E are shown in Table 7.

It was observed earlier [1,2] that the derived Arrhenius parameters (E and A), as calculated by various methods for different heating rates, follow a linear relationship viz.

$$\ln A = aE + b \tag{3}$$

TABLE 6

Results of analysis of densification kinetic data for 20 Silver compacts according to the differential method. The Ginstling–Brounshtein equation is used as governing rate equation [f(α)]

Compact no.	β (K $\min^{-1}$)	E (kJ mole^{-1})	A (Hz)	Correlation coefficient	Variance
Ag/1	5	156.94	0.1749 E+04	0.937	0.07591
Ag/2	5	174.95	0.1286 E+05	0.920	0.13789
Ag/3	5	143.45	0.1434 E+03	0.929	0.11395
Ag/4	5	141.13	0.2176 E+03	0.936	0.06797
Ag/5	10	241.56	0.1426 E+09	0.984	0.03929
Ag/6	10	149.21	0.1688 E+04	0.936	0.06740
Ag/7	10	179.93	0.6051 E+05	0.976	0.03620
Ag/8	10	181.92	0.7711 E+05	0.973	0.04281
Ag/9	15	164.31	0.1182 E+05	0.959	0.05615
Ag/10	15	141.03	0.3136 E+03	0.953	0.07186
Ag/11	15	179.85	0.5714 E+05	0.946	0.10533
Ag/12	15	180.26	0.5962 E+05	0.947	0.10451
Ag/13	20	141.20	0.6346 E+03	0.947	0.06859
Ag/14	20	143.84	0.6530 E+03	0.957	0.06659
Ag/15	20	149.83	0.1817 E+04	0.959	0.05896
Ag/16	20	135.67	0.2991 E+03	0.949	0.06467
Ag/17	25	171.80	0.1561 E+05	0.954	0.06092
Ag/18	25	135.02	0.1033 E+03	0.946	0.06614
Ag/19	25	226.38	0.3000 E+07	0.974	0.08416
Ag/20	25	170.65	0.6234 E+04	0.979	0.03798

where a and b are constants.

This is known as the kinetic compensation effect which is typical for non-isothermal processes. In this case also, it was observed that such a linear relationship is valid. The calculated values of E and A were fitted to eqn. (3) by the linear least-squares method and the results are shown in Table 8. The calculated values of T_c (i.e. the so-called characteristic temperature) fall within the experimental temperature ranges.

CONCLUSIONS

The new mathematical method of analysis of non-isothermal densification data of various types of powder compacts seems to be applicable in the present case also. It is observed that no single known functional form of g(α) is suitable for describing the entire range of densification. However, the initial period ($\alpha = 0.3$) may be described very nicely by a three-dimensional diffusion-controlled process. During the later stage of densification, grain-

TABLE 7

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

Compact no.	β (K min^{-1})	E (kJ $mole^{-1}$)	Correlation coefficient	Variance
Ag/1	5	162.19	0.915	0.11475
Ag/2	5	177.12	0.894	0.29121
Ag/3	5	144.92	0.903	0.17254
Ag/4	5	153.03	0.921	0.10371
Ag/5	10	204.96	0.961	0.06614
Ag/6	10	167.57	0.928	0.09549
Ag/7	10	158.97	0.948	0.06439
Ag/8	10	161.86	0.943	0.07324
Ag/9	15	163.97	0.935	0.09161
Ag/10	15	136.24	0.924	0.11428
Ag/11	15	175.65	0.918	0.16023
Ag/12	15	176.21	0.918	0.15990
Ag/13	20	137.45	0.918	0.10472
Ag/14	20	135.28	0.925	0.10906
Ag/15	20	145.79	0.931	0.09645
Ag/16	20	132.45	0.920	0.10013
Ag/17	25	174.59	0.934	0.09251
Ag/18	25	133.47	0.910	0.11429
Ag/19	25	184.96	0.944	0.12904
Ag/20	25	152.85	0.942	0.09167

growth phenomena and other related structural changes become predominant and hence make the process too complicated to be described by only one rate law.

The values of the derived Arrhenius parameters (i.e. E and A) were calculated and it was noted that they are very much dependent upon the rate of heating and also on the method of calculation. Therefore, it is confirmed

TABLE 8

Kinetic compensation effect: $\ln A = aE + b$. Results of linear least-squares fitting. Here, $T_c = 1/Ra$

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 4	0.1269	−11.3097	0.977	0.28943	947.67
Integral	Table 5	0.1204	−14.9315	0.982	0.57529	998.81
Differential	Table 6	0.1211	−11.1925	0.984	0.41303	993.05

once again that it would be futile to assign a particular mechanism to a process by only considering the values of the derived Arrhenius parameters.

Establishment of the well-known kinetic compensation effect may be taken to be indirect proof of the validity of the present method. The actual significance is, however, not very clear yet.

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