KINETICS OF THE DENSIFICATION OF SILVER POWDER COMPACTS DURING NON-ISOTHERMAL SOLID-STATE SINTERING. A PHENOMENOLOGICAL APPROACH

T.P. BAGCHI and P.K. SEN

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

(Received 12 February 1983)

ABSTRACT

The handling of a complete range of densification kinetic data of non-isothermal sintering by the well-established method of thermal analysis is a difficult task because several simultaneous and/or sequential mechanisms come into play during the course of sintering. No fruitful mathematical method has yet been reported in the literature to separate out the individual mechanisms, especially when there is a transition from one mechanism to another or when, in a small range of densification, the process is governed by a mixed mechanism. To tackle this problem, a phenomenological equation, which would aptly describe the non-isothermal densification kinetics of commercial silver powder compacts for a high degree of densification ($\alpha \approx 0.6$–0.7), has been proposed.

Experimental data were fitted to this equation and the derived Arrhenius parameters (E and A) were thus calculated. The kinetic compensation effect is also seen to be valid.

INTRODUCTION

When a porous green powder compact is exposed to elevated temperatures, it becomes densified; this phenomenon is commonly known as 'sintering', and is a complex process. Although an enormous fund of knowledge regarding the behaviour of powder particles during sintering is available at present, the fundamental knowledge of the mechanism of sintering still remains as a matter of controversy. Constant attempts are being made to establish a generalized and unified theory of sintering which would encompass almost all major aspects of sintering however complicated and diversified they may be. While many theoreticians have kept themselves busy on the fundamental aspects of the sintering process assuming simple geometrical models, there is a good number of pragmatic powder metallurgists who are trying to visualize the whole process a posteriori from a practical point of view and, as a result of their constant endeavours, various types of empirical and semi-empirical shrinkage equations are available in the literature. These potential shrinkage equations are not always limited by oversimplified

assumptions regarding the shapes and sizes of the particles of the powder. These shrinkage equations are very useful to practical powder metallurgists for comparing the sinterabilities of different grades of commercial powders.

Some authors have also tried to explain the phenomenological equations, proposed by them, from theoretical standpoints in order to bridge the obvious gap between theoretical knowledge and its practical application. These attempts, however, could not contribute anything significant to the understanding of the fundamentals of the sintering process. Various aspects of the phenomenological approach have been critically assessed by Exner [1–3].

Different types of simple isothermal phenomenological shrinkage equations have been proposed, some of which have been tabulated by Thümmler and Thomma [4]. The objective of the present paper, however, is to develop a generalized and non-mechanistic shrinkage equation for describing the kinetics of the densification of commercial powder compacts during solid-state sintering under non-isothermal conditions and also to calculate the values of the derived Arrhenius parameters (E and A) of the densification process.

THEORETICAL CONSIDERATIONS

Densification parameter (α)

A green powder compact is essentially composed of two different phases: (i) pores and (ii) solid material. While being sintered, the pores gradually become annihilated and thus the compact becomes densified; according to Hirschhorn [5,6] the subject of sintering is best approached from this view point. The process of sintering has also been viewed from this direction by Thümmler [7] who has defined the term "sintering" as "a thermally activated mass transport reinforcing particle contacts and/or changing pore geometry. A liquid phase can participate in the process."

Hausner and Duzevic [7], in supporting this idea, made an interesting comment on this type of definition. "'Some-thing' and 'no-thing' both are parts of the reality. The powder metallurgists tend to operate mainly with the solid matter in the mass of powder which they consider to be the 'real-thing' and usually neglect in their thinking the second component in the powder mass, the 'no-thing'—the voids or pores.

During sintering many changes occur in the powder particles, but more changes still occur in the pore structure. The mass of particles is practically the same after sintering as before; the porosity, however, undergoes changes in size, shape, number of pores and in total pore volume. The final aim of sintering frequently is the complete elimination of porosity. The sintering process can be perfectly described in terms of porosity and pore characteris-

tics, i.e. by the decrease in surface area inside of the powder mass."

This concept is the theoretical foundation of the present work, where the kinetics of densification of a powder compact during sintering are expressed by the rate at which the pores of the powder compact become annihilated during sintering. The degree of densification is suitably expressed with the help of a densification parameter (α) where

$$\alpha = 1 - \frac{v_s}{v_p} = \frac{V_p - V_s}{V_p - V_{th}} = \frac{1 - (V_s/V_p)}{1 - (V_{th}/V_p)} = \frac{1 - (V_s/V_p)}{1 - (\rho_p/\rho_{th})} = \frac{1 - (V_s/V_p)}{P} \tag{1}$$

where,

v_s = volume of pores in the sintered compact,
v_p = volume of pores in the green compact,
V_{th} = volume of the compact when it attains its theoretical density (ρ_{th}) after complete annihilation of pores,
V_p = volume of the green compact ($V_{th} + v_p$),
V_s = volume of the sintered compact ($V_{th} + v_s$),
ρ_p = density of the green compact, and
P = porosity of the green compact
= $1 - (\rho_p/\rho_{th})$.

A similar type of densification parameter was suggested previously by Tikkanen and Mäkipirtti [8] for studying the isothermal kinetics of densification of various powder compacts. This type of densification parameter also proved to be useful in describing the densification (early stage) behaviour of powder compacts during sintering under non-isothermal conditions [9–12].

When a small cylindrical compact is sintered inside a furnace, its longitudinal contraction (ΔL) may be registered at different times (t) by the usual dilatometric method. The value of the ratio (V_s/V_p) at any time (t) is calculated using the approximate relationship [9]

$$\frac{V_s}{V_p} = \left(1 - \frac{\Delta L}{L_0}\right)\left(1 - \frac{\Delta D_f}{\Delta L_f} \times \frac{\Delta L}{D_0}\right)^2 \tag{2}$$

where,

ΔL = longitudinal contraction of the compact as recorded by the dilatometer,
L_0 = length of the green compact,
D_0 = diameter of the green compact,
ΔD_f = final change in the lateral direction of the compact, and
ΔL_f = final change in the longitudinal direction of the compact.

Using this value of (V_s/V_p), the value of α at any temperature (T) and time (t) is calculated with the help of eqn. (1).

Phenomenological shrinkage equation

It was shown [10–12] that the early stage of densification (i.e. up to $\alpha \simeq 0.3$) process was governed by the Ginstling–Brounshtein equation which indicated a three-dimensional diffusion-controlled process. But for higher degrees of densification (i.e. up to $\alpha \simeq 0.7$), no single known form of rate law [i.e. g(α)], as tabulated elsewhere [9], was suitable for describing the non-isothermal densification process [11,12]. At this stage of densification, grain-growth phenomena and other related mechanisms came into play which possibly made the whole process too complex to be described by a single known rate law. It was, therefore, felt necessary to develop a phenomenological shrinkage equation for the entire experimental range of densification of the powder compacts. For non-isothermal densification studies, the following type of densification equation was found to be suitable (in accordance with the thermodynamical approach)

$$\alpha^z = kt \tag{3}$$

where,

z = reaction exponent,
k = reaction constant, and
t = time of sintering.

The rate constant (k) of the process is assumed to be related to the temperature of sintering (T) as per an Arrhenius-type relationship

$$k = A \exp(-E/RT) \tag{4}$$

where

A = derived frequency factor (Hz),
E = derived activation energy (kJ mole^{-1}),
T = sintering temperature (K), and
R = universal gas constant (0.0083143 kJ K^{-1} mole^{-1}).

Sintering time (t) is also related to the sintering temperature (T); for a linear rate of heating (β)

$$t = \frac{T - T_0}{\beta} \tag{5}$$

where T_0 = onset temperature of densification.

Combining eqns. (3), (4) and (5) gives

$$\alpha^z = \left(\frac{A}{\beta} \right) \exp(-E/RT)(T - T_0) \tag{6}$$

Taking logarithms of both sides and rearranging the terms

$$z \ln \alpha - \ln(T - T_0) = \ln(A/\beta) - (E/RT) \tag{7}$$

Equation (7) is thus the final expression for the densification of powder compacts during non-isothermal single-phase sintering. There are three inde-

pendent adjustable parameters (viz. E, A and z) in this expression. The value of the exponent (z) is to be adjusted tacitly so as to fit the experimental data (i.e. α vs. T) to eqn. (7) by the usual linear least-squares method with a reasonably good degree of accuracy whilst yielding logically acceptable values of the derived Arrhenius parameters (E and A). This, of course, is to be done by trial-and-error method. The necessary computer program [in FORTRAN IV] has been developed for this purpose.

The results of analysis of non-isothermal densification kinetic data (up to $\alpha \simeq 0.3$) of 20 silver powder compacts were published earlier [12]; here, the non-isothermal densification kinetic data (up to $\alpha \simeq 0.6$–0.7) of those 20 silver powder compacts are reanalysed with the help of the phenomenological approach [i.e. eqn. (7)].

EXPERIMENTAL

Twenty silver powder compacts were sintered at five different linear heating rates ($\beta = 5$, 10, 15, 20 and 25 K min^{-1}). Details of compaction and sintering schedules have been published elsewhere [12]. Other information

TABLE 1

Values of β, T_0, T_f, t_f and α_m for 20 silver powder compacts

Compact No.	β (K min^{-1})	T_0 (K)	T_f (K)	t_f (s)	α_m
Ag/1	5	873	1173	3600	0.646387
Ag/2	5	873	1173	3600	0.689563
Ag/3	5	873	1173	3600	0.643138
Ag/4	5	873	1173	3600	0.635402
Ag/5	10	873	1173	1800	0.712532
Ag/6	10	873	1173	1800	0.715181
Ag/7	10	873	1173	1800	0.707488
Ag/8	10	873	1173	1800	0.709657
Ag/9	15	873	1173	1200	0.662441
Ag/10	15	873	1173	1200	0.587405
Ag/11	15	873	1173	1200	0.666265
Ag/12	15	873	1173	1200	0.664592
Ag/13	20	873	1173	900	0.694673
Ag/14	20	873	1173	900	0.658099
Ag/15	20	873	1173	900	0.673049
Ag/16	20	873	1173	900	0.677167
Ag/17	25	923	1173	600	0.570902
Ag/18	25	923	1173	600	0.545434
Ag/19	25	923	1173	600	0.547158
Ag/20	25	923	1173	600	0.536406

regarding particle size, dimensions of the green compact and the sintered compacts are given in tables 1–3 of ref. 12.

RESULTS AND DISCUSSION

Calculation of the derived Arrhenius parameter (E *and* A)

From the recorded values of ΔL, the values of α, at different times (t) and temperatures (T), were calculated for each silver powder compact. The values of T_0, T_f and t_f and the calculated values of α_m are tabulated in Table 1 (for 20 compacts), where

$T_0 =$ onset temperature of densification (K),
$T_f =$ temperature up to which the compact was heated (K),
$t_f =$ total time of densification (s)
$\quad = (T_f - T_0)/\beta$, and
$\alpha_m =$ value of the densification parameter at temperature T_f.

A typical α vs. T plot (for compact No. Ag/1, $\beta = 5$ K min^{-1}) is shown in Fig. 1. These kinetic data were fitted to eqn. (7) by linear least-squares method with different arbitrary values of z and the corresponding Arrhenius parameters were calculated therefrom. The results are shown in Table 2. The values of the Arrhenius parameters are quite acceptable for $z = 3.0$; the accuracy of the corresponding least-squares fitting is also reasonably good.

In a similar fashion, the non-isothermal densification kinetic data, as obtained for the remaining 19 silver powder compacts (numbered as: Ag/2, Ag/3,..., Ag/20), were analysed for different arbitrary values of z. It was
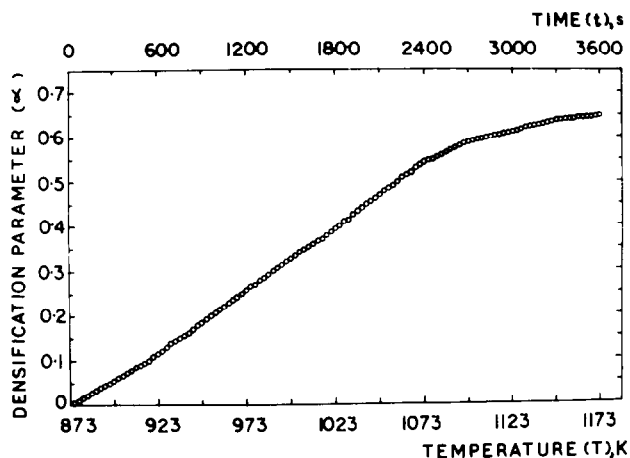

Fig. 1. A plot of the densification parameter (α) vs. temperature (T) and time (t). Compact No. Ag/1; heating rate (β) = 5 K min^{-1}.

TABLE 2

Values of the derived Arrhenius parameters (E and A) for different values of z [compact No. Ag/1; heating rate (β) = 5 K min^{-1}]

z	E (kJ mole^{-1})	$\ln(A)$	Linear correlation coefficient	Variance
0.2	− 67.13	− 15.4104	0.922	0.0878
0.4	− 49.81	− 13.6162	0.927	0.0462
0.6	− 32.48	− 11.8202	0.934	0.0188
0.8	− 15.18	− 10.0282	0.934	0.0050
1.0	2.15	− 8.2320	0.266	0.0055
1.2	19.44	− 6.4411	0.810	0.0198
1.4	36.74	− 4.6490	0.859	0.0487
1.6	54.04	− 2.8570	0.875	0.0912
1.8	71.34	− 1.0650	0.883	0.1486
2.0	88.66	0.72930	0.887	0.2192
2.2	105.93	2.5180	0.890	0.3053
2.4	123.23	4.3101	0.892	0.4049
2.6	140.53	6.1021	0.894	0.5187
2.8	157.83	7.8952	0.895	0.6463
3.0	175.13	9.6862	0.896	0.7885
3.2	192.39	11.4738	0.897	0.9460
3.4	209.71	13.2681	0.898	1.1158
3.6	227.01	15.0601	0.898	1.3005
3.8	244.31	16.8621	0.899	1.4992
4.0	261.62	18.6453	0.899	1.7118
4.2	278.95	20.4407	0.899	1.9375
4.4	296.23	22.2305	0.900	2.1794
4.6	313.51	24.0203	0.900	2.4363
4.8	330.84	25.8157	0.900	2.7040
5.0	348.18	27.6122	0.900	2.9848
5.2	365.43	29.3987	0.901	3.2862
5.4	382.75	31.1929	0.901	3.5966
5.6	400.06	32.9861	0.901	3.9220
5.8	417.36	34.7792	0.901	4.2615
6.0	434.74	36.5801	0.901	4.6096
6.2	452.01	38.3688	0.901	4.9805
6.4	469.35	40.1653	0.901	5.3593
6.6	486.60	41.9518	0.901	5.7606
6.8	503.91	43.7450	0.902	6.1708
7.0	521.20	45.5359	0.902	6.5970
7.2	538.57	47.3357	0.902	7.0288
7.4	555.87	49.1277	0.902	7.4823
7.6	573.17	50.9198	0.902	7.9496
7.8	590.46	52.7118	0.902	8.4314
8.0	607.79	54.5072	0.902	8.9234
8.2	625.03	56.2915	0.902	9.4420
8.4	642.35	58.0869	0.902	9.9620
8.6	659.68	59.8822	0.902	10.4965
8.8	677.04	61.6809	0.902	11.0407

TABLE 2 (continued)

z	E (kJ mole^{-1})	$\ln(A)$	Linear correlation coefficient	Variance
9.0	694.31	63.4696	0.902	11.6105
9.2	711.32	65.2606	0.902	12.1934
9.4	728.96	67.0593	0.903	12.7802
9.6	746.27	68.8524	0.903	13.3866
9.8	763.57	70.6445	0.903	14.0097
10.0	780.87	72.4365	0.903	14.6462

N.B. A is expressed in Hz.

observed in each case that acceptable values of the Arrhenius parameters were obtained (along with a high accuracy of linear least-squares fitting of the experimental data) when $z = 3.0$. Therefore, the final expression of the phenomenological equation, which was applicable in this case, became

$$3 \ln \alpha - \ln(T - T_0) = \ln(A/\beta) - (E/RT) \tag{8}$$

The experimental data, as obtained for 20 compacts (i.e. No. Ag/1, Ag/2,..., Ag/20], were then fitted to eqn. (8) and the results obtained are tabulated in Table 3. In each case, the accuracy of least-squares fitting is very high.

Kinetic compensation effect

It was observed earlier [10–12] that the derived Arrhenius parameters (E and A), as calculated by the analysis of the non-isothermal densification
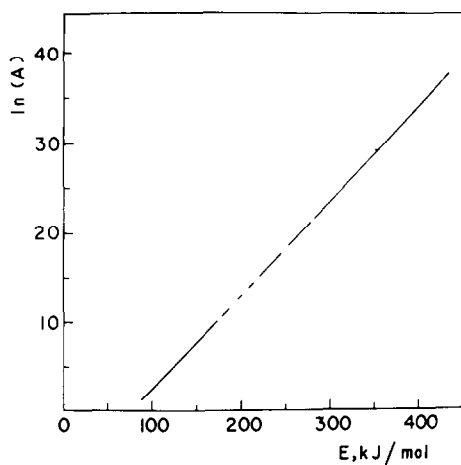

Fig. 2. Kinetic compensation plot (results of linear least-squares fitting). ln $A = 0.106665$ $E - 8.257303$.

TABLE 3

Results of analysis of the non-isothermal densification kinetic data of 20 silver powder compacts using a phenomenological equation [eqn. (8)]

Compact No.	Heating rate (K min^{-1})	E (kJ mole^{-1})	ln (A)	Linear correlation coefficient	Variance
Ag/1	5	175.13	9.6862	0.896	0.7885
Ag/2	5	202.72	12.6716	0.883	1.2240
Ag/3	5	217.18	13.8100	0.918	0.9272
Ag/4	5	166.34	8.4274	0.898	0.6964
Ag/5	10	214.02	15.0258	0.895	1.1889
Ag/6	10	174.89	10.6572	0.900	0.7482
Ag/7	10	190.12	12.2640	0.923	0.6515
Ag/8	10	192.46	12.5318	0.920	0.6981
Ag/9	15	188.92	12.3234	0.909	0.7760
Ag/10	15	203.71	13.2336	0.924	0.7351
Ag/11	15	222.77	15.9752	0.902	1.1819
Ag/12	15	223.40	16.0361	0.902	1.1895
Ag/13	20	188.80	12.2831	0.929	0.5859
Ag/14	20	205.65	13.9354	0.932	0.6674
Ag/15	20	204.25	14.1402	0.933	0.6395
Ag/16	20	188.13	12.1281	0.932	0.5569
Ag/17	25	244.74	18.1858	0.927	0.6378
Ag/18	25	251.43	18.2763	0.947	0.4697
Ag/19	25	351.97	29.1658	0.949	0.8785
Ag/20	25	280.75	21.4084	0.950	0.5474

N.B. A is expressed in Hz.

kinetic data of different types of powder compacts, follow a definite linear relationship of the form

$$\ln(A) = aE + b \tag{9}$$

where a and b are constants.

This is commonly known as the 'kinetic compensation effect (KCE)' which was observed in many non-isothermal processes [13,14]. In the present case also, such a linear relationship was seen to be valid. The equation to this straight line, as obtained by linear least-squares method (with linear correlation coefficient = 0.993 and variance = 0.3006), is

$$\ln(A) = 0.106665E - 8.257303 \tag{10}$$

and this linear plot is shown in Fig. 2.

Garn [15,16] has defined a 'characteristic temperature (T_c)' which is related to the slope (a) of the linear compensation plot

$$T_c = 1/(Ra) \tag{11}$$

In the present case

$T_c = 1/(0.0083143 \times 0.106665)$ K

or

$T_c = 1127.6$ K

The value of T_c falls within the experimental temperature range (873–1173 K) of sintering. Since the physical significance of the derived Arrhenius parameters for heterogeneous systems (especially under non-isothermal conditions) is not yet explicitly established, the exact reason behind such a compensation relationship is not understood completely.

CONCLUSIONS

The proposed phenomenological approach for analysing the non-isothermal densification kinetic data (up to $\alpha \simeq 0.6$–0.7) of commercial silver powder compacts is useful for calculating the values of the derived Arrhenius parameters (E and A). This type of shrinkage equation is unavoidable, since no other explicit mathematical relationship, covering all fundamental aspects of the non-isothermal sintering of commercial powder compacts (with particles of irregular shape and size), is available in the literature. The proposed phenomenological equation is, however, purely non-mechanistic in nature and cannot contribute any important information to the present state of knowledge of the physical nature of the sintering process from a strictly theoretical standpoint.

The values of the derived Arrhenius parameters (E and A) are obtained by fitting the experimental data to the phenomenological equation and, therefore, these parameters are to be regarded as nothing more than two fitted parameters with limited validity and unknown physical significance. It would be futile to conclude anything regarding the mechanism of the process by considering the values of z, E and A.

The values of these derived Arrhenius parameters are dependent upon the heating rate. Even for the same heating rate, their values may be different for different compacts; this variation may be due to the fact that the morphology of pores of one compact is never identical to that of another.

The kinetic compensation effect is seen to be valid in the present case but its theoretical significance is not understood completely.

REFERENCES

1 H.E. Exner, Rev. Powder Metall. Phys. Ceram., 1 (1979) 186.
2 H.E. Exner, Powder Metall., 4 (1980) 203.
3 H.E. Exner and G. Petzow, in G.C. Kuczynski (Ed.), Sintering Processes, Plenum, New York, 1980, p. 107.

4 F. Thummler and W. Thomma, Metall. Rev., 12 (1967) 69.
5 J.S. Hirschhorn, Introduction to Powder Metallurgy, American Powder Metallurgy Institute, New York, 1969, p. 155.
6 J.S. Hirschhorn, in M.M. Ristić (Ed.), Science of Sintering and Its Future, International Institute for the Science of Sintering, Beograd, Yugoslavia, 1975, p. 19.
7 H.H. Hausner and D. Duzević, Sci. Sintering, 12 (2) (1980) 137.
8 M.H. Tikkanen and S.A. Mäkipirtti, Intl. J. Powder Metall., 1(1) (1965) 15.
9 T.P. Bagchi and P.K. Sen, Thermochim. Acta, 56 (1982) 261.
10 T.P. Bagchi and P.K. Sen, Thermochim. Acta, 56 (1982) 269.
11 T.P. Bagchi and P.K. Sen, Thermochim. Acta, 61 (1983) 73.
12 T.P. Bagchi and P.K. Sen, Thermochim. Acta, 61 (1983) 87.
13 P.K. Gallagher and D.W. Johnson, Jr., Thermochim. Acta, 14 (1976) 255.
14 J. Zsakó, J. Therm. Anal., 9 (1976) 101.
15 P.D. Garn, J. Therm. Anal., 7 (1975) 475.
16 P.D. Garn, J. Therm. Anal., 10 (1976) 99.