

## KINETICS OF DENSIFICATION OF POWDER COMPACTS DURING THE INITIAL STAGE OF SINTERING WITH CONSTANT RATES OF HEATING. A THERMAL ANALYSIS APPROACH. PART I. THEORETICAL CONSIDERATIONS

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### ABSTRACT

Densification of powder compacts during sintering (initial stage) under constant heating rate has been studied and methods of analysing the densification kinetic data have been suggested.

Green compacts can broadly be envisaged to consist of two phases, viz porosity and solid material. Annihilation of the pores causes densification of the compacts during sintering. So, the kinetics of the initial stage of densification may very well be represented by a densification parameter ( $\alpha$ ), where

$$\alpha = 1 - (v_s/v_p)$$

Here,  $v_s$  and  $v_p$ , respectively, denote the pore volumes of the sintered and the green compact. Continuous and in situ recording of the linear shrinkage ( $\Delta L$ ) of the compacts during sintering may be done with a dilatometer and using this value of  $\Delta L$ , the value of  $\alpha$  at any temperature ( $T$ ) may be calculated.

These kinetic data ( $\alpha$  vs  $T$ ) may then be subjected to analysis using the well-known methods of thermal analysis, and the so-called “derived activation energy ( $E$ )” of densification may be evaluated therefrom. The exact form of  $g(\alpha)$ —governing rate equation—is ascertained by a trial-and-error method.

These methods were used to analyse the densification kinetic data of haematite, copper and silver powders (with particles of irregular shapes and sizes). The results of such analyses will appear in other parts of this paper.

### INTRODUCTION

Because of its complex nature, study of the kinetics of densification and/or shrinkage of powder compacts during sintering constitutes a fascinating area of research in the field of powder metallurgy and ceramics [1]. Model studies, with particles of definite geometry, have been carried out by Kuczynski [2] and others under strictly isothermal conditions. These fundamental studies are of enormous theoretical importance, but the conclu-

sions drawn from such types of isothermal and over-simplified model studies can hardly be extrapolated to predict the sintering behaviour of real powder systems because of their inherent limitations, notably their inability to account for the densification process during the heat-up period. Further, simplified assumptions regarding the particle geometry make these studies almost useless for throwing light on the densification characteristics of real powder systems with wide variations in particle shapes and sizes.

To circumvent the first limitation, studies on non-isothermal sintering [especially, under constant rate of heating (CRH)] are gradually attracting the attention of many research workers. CRH experiments have proved to be a very useful tool to study the densification behaviour of the powder compacts during the heat-up period with a programmed rate of heating.

Study of the process of sintering under non-isothermal conditions dates back to the early 1950s [3–5], but little has been done to relate the experimental results to sintering mechanisms. Herman's [6] studies on the sintering behaviour of pure metal spheres resulted in a mathematical method of analysis with due considerations to the sintering mechanism. Later, various methods of calculation of non-isothermal sintering data were proposed by Cutler [7–10], Johnson et al. [11–16] and Ristić et al. [17]. But all these methods of calculation, incorporating average particle radius in the rate equations, are applicable only for the sintering of uniformly sized spherical particles and are of hardly any use for kinetic calculations of non-isothermal densification data obtained during sintering of real powder systems with particles of irregular shapes and sizes, where initial average particle radius is unpredictable.

The present work was undertaken to study the initial stage of densification during sintering (under CRH) of various metallic and oxide systems with particles of irregular shapes and sizes, a case close to the actual sintering process encountered in practice. Mathematical methods for determination of the so-called "derived activation energy ( $E$ )" of densification have been proposed. These methods have their basis in the well-known methods of thermal analysis which have been used extensively for analysing the non-isothermal kinetic data of various solid-state reactions. It is seen that the non-isothermal densification data obtained during sintering, which itself is a thermally-activated solid-state process (with no chemical reaction involved) are also amenable to such types of analysis.

## PRESENT METHOD OF ANALYSIS

A porous compact is thermodynamically unstable and, when exposed to elevated temperatures, it tends to agglomerate in order to reduce the volume of the pores. When a green compact is heated up, contacts are formed between the adjacent particles and thus the pores present in the compact

form an almost continuous phase. In the porous compacts, the capillary forces act to reduce the porosity ( $P$ ) while being sintered. The action of the capillary forces may be expressed as a hydrostatic pressure which acts on the compacts from outside. Under the action of this pressure, vacancies migrate from the vacancy source (i.e. pore phase) to the vacancy sink (i.e. matrix) and are absorbed there. This, in other words, means that an equivalent amount of atom movement takes place in the opposite direction (i.e. from the matrix to the pores) and the pores get filled up [18]. This indicates that the rate of densification may very well be represented by the rate of annihilation of pores present in the compact during sintering.

Hirschhorn [19], in supporting this idea, has observed "The subject of sintering is best approached from the view point that any green compact or press of loose powder is at the very least a two phase material—porosity and solid material. Each has its own morphology; that is, size, shape, distribution and amount".

Bearing this in mind, it is possible to define a densification parameter ( $\alpha$ ) (which denotes the extent of densification that has taken place) as

$$\begin{aligned} \alpha &= 1 - \frac{v_s}{v_p} = \frac{v_p - v_s}{v_p} = \frac{V_p - V_s}{V_p - V_{th}} = \frac{1 - (V_s/V_p)}{1 - (V_{th}/V_p)} = \frac{1 - (V_s/V_p)}{1 - (\rho_p/\rho_{th})} \\ &= \frac{1 - (V_s/V_p)}{P} \end{aligned} \quad (1)$$

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 ( $\rho_{th}$ ) after complete densification,  $V_p$  = volume of the green compact ( $V_{th} + v_p$ ),  $V_s$  = volume of the sintered compact ( $V_{th} + v_s$ ),  $\rho_p$  = density of the green compact,  $P$  = porosity of the green compact =  $1 - (\rho_p/\rho_{th})$ .

This type of densification parameter was suggested earlier by Tikkanen and Mäkipirtti [20].

When the compact is sintered inside a furnace, continuous and in situ recording of any instantaneous change in its length ( $\Delta L$ ) may be done with the help of a dilatometer. The value of  $V_s$  may be calculated from the recorded value of  $\Delta L$  using the approximate relationship suggested by Ivensen [21] incurring an error level of 3% (maximum). The relationship between  $(V_s/V_p)$  and  $(\Delta L/L_0)$  is given by

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

where,  $\Delta D_f$  and  $\Delta L_f$  are the final changes in the lateral direction and longitudinal direction respectively.  $D_0$  and  $L_0$ , respectively, denote the diameter and length of the green compact (assumed to be cylindrical).

With this calculated value of  $(V_s/V_p)$ , the value of  $\alpha$  at any time ( $t$ ) and temperature ( $T$ ) may be calculated using eqn. (1). These data ( $\alpha$  vs.  $T$ ) may then be analysed according to the following methods of thermal analysis, viz. (i) Ingraham's method [22], (ii) Coats and Redfern's method [23], and (iii) combined integral and differential method [24]. The methods are briefly outlined below.

*(i) Ingraham's method [22]*

The mathematical form of the relationship suggested by Ingraham is given by

$$\ln\left(\frac{\beta\alpha}{T^3}\right) = -\frac{E}{RT} + \text{constant} \quad (3)$$

where  $\beta$  = constant rate of heating,  $T$  = temperature,  $E$  = derived activation energy,  $R$  = universal gas constant ( $8.3143 \text{ J K}^{-1} \text{ mole}^{-1}$ ).

So, a plot of  $\ln(\beta\alpha/T^3)$  vs.  $1/T$  is expected to be a straight line, whose slope will give the value of  $E$ . This method, however, is incapable of predicting the reaction mechanism.

*(ii) Coats and Redfern's method [23]*

This relationship, proposed by Coats and Redfern, is given by

$$\ln[g(\alpha)/T^2] = (-E/RT) + \ln[(AR/\beta E)(1 - 2RT/E)] \quad (4)$$

where  $E$  = derived activation energy,  $A$  = derived frequency factor,  $g(\alpha)$  = a kinetic function of  $\alpha$  which denotes the reaction mechanism operative (cf. Table 1).

For a not-too-wide temperature range of study, the term  $\ln[(AR/\beta E)(1 - 2RT/E)]$  may be assumed to be fairly constant. So, a plot of  $\ln[g(\alpha)/T^2]$  vs.  $(1/T)$  is expected to give a straight line fit of the experimental data if the proper functional form of  $g(\alpha)$  is chosen. The slope and intercept of the resulting straight line will give the value of  $E$  and that of  $A$ , respectively. The exact form of  $g(\alpha)$  is ascertained by a trial-and-error method.

*(iii) Combined Integral and Differential Method [24]*

This method is suitable for pin-pointing the most probable form of  $g(\alpha)$  which is followed by the process under study. The integral form of the relationship is

$$\ln g(\alpha) - \ln(T - T_0) = \ln(A/\beta) - E/RT \quad (5)$$

where  $T_0$  denotes the temperature at which measurable shrinkage begins.

A plot of  $[\ln g(\alpha) - \ln(T - T_0)]$  vs.  $(1/T)$  will be a straight line and as

TABLE I  
Different kinetic functions  $g(\alpha)$  and  $f(\alpha)$  used in the present analysis

Function no.	Name	$g(\alpha)$	$f(\alpha)$
1	Parabolic law (diffusion, 1D)	$\alpha^2$	$1/(2\alpha)$
2	Valensi (Barrer) equation (diffusion, 2D)	$\alpha + (1-\alpha) \ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$
3	Ginstling-Brounshtein equation (diffusion, 3D)	$(1-\frac{2}{3}\alpha) - (1-\alpha)^{2/3}$	$\frac{2}{3}[(1-\alpha)^{-1/3} - 1]^{-1}$
4	Jander equation (diffusion, 3D)	$[1 - (1-\alpha)^{1/3}]^2$	$\frac{2}{3}(1-\alpha)^{2/3} [1 - (1-\alpha)^{1/3}]^{-1}$
5	Avrami-Erofeev equation (N and G)	$[-\ln(1-\alpha)]^{2/3}$	$\frac{2}{3}(1-\alpha) [-\ln(1-\alpha)]^{1/3}$
6	Avrami-Erofeev equation (N and G)	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha) [-\ln(1-\alpha)]^{1/2}$
7	Avrami-Erofeev equation (N and G)	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha) [-\ln(1-\alpha)]^{2/3}$
8	Avrami-Erofeev equation (N and G)	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha) [-\ln(1-\alpha)]^{3/4}$
9	Contracting geometry (cylindrical symmetry)	$1 - (1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
10	Contracting geometry (spherical symmetry)	$1 - (1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
11	Mampel power law	$\alpha$	1
12	Mampel power law	$\alpha^{1/2}$	$2\alpha^{1/2}$
13	Mampel power law	$\alpha^{1/3}$	$3\alpha^{2/3}$
14	Mampel power law	$\alpha^{1/4}$	$4\alpha^{3/4}$
15	Chemical reaction (1st order)	$-\ln(1-\alpha)$	$(1-\alpha)$
16	Chemical reaction (2nd order)	$(1-\alpha)^{-1} - 1$	$(1-\alpha)^2$
17	Chemical reaction (1.5th order)	$(1-\alpha)^{-1/2} - 1$	$2(1-\alpha)^{3/2}$

before  $E$  and  $A$  may be calculated from its slope and intercept, respectively.

The differential relationship is given by

$$\ln \left[ \frac{(d\alpha/dT)}{\{ [E(T - T_0)/RT^2] + 1 \} f(\alpha)} \right] = \ln (A/\beta) - (E/RT) \quad (6)$$

$$\text{where, } f(\alpha) = 1/g'(\alpha) \quad (6a)$$

This non-linear equation may be solved by an iterative method as discussed elsewhere [24].

The actual forms of  $g(\alpha)$  and  $f(\alpha)$  are ascertained by logical discrimination. Different functional forms of  $g(\alpha)$  and  $f(\alpha)$  for different reaction mechanisms are given in Table I.

These methods are used to analyse the densification kinetic data of haematite compacts which were sintered up to a volume shrinkage ( $\Delta V/V_0$ ) of  $\sim 12\%$  which corresponds to  $\alpha \sim 0.3$ . The experimental procedure and results will appear in Part II of this paper.

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