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Master Sintering Curve – A Practical Approach to its Construction

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Abstract:
The concept of a Master Sintering Curve (MSC) is a strong tool for optimizing the sintering process. However, constructing the MSC from sintering data involves complicated and time- consuming calculations. A practical method for the construction of a MSC is presented in the paper. With the help of a few dilatometric sintering experiments the newly developed software calculates the MSC and finds the optimal activation energy of a given material. The software, which also enables sintering prediction, was verified by sintering tetragonal and cubic zirconia, and alumina of two different particle sizes.
Keywords*: Alumina, Zirconia, Sintering, MSC, Densification prediction*

Introduction

Sintering is a thermally activated process with the development of bonds between particles as a result of the motion of atoms and ions, together with the reduction of porosity. Since the motion of atoms and ions in solids is generally realized via diffusion, there is a strong dependence of sintering on temperature. One of the promising methods how to describe and predict sintering is the concept of a Master Sintering Curve (MSC) developed by Su and Johnson [1].

MSC is derived from the sintering theory proposed by Hansen and co-workers [2]. The model relates the linear shrinkage rate of a compact to grain boundary and volume diffusion coefficient, surface tension and microstructure variables:

$$-\frac{dL}{Ldt}=\frac{\gamma\Omega}{kT}\left(\frac{\Gamma_v D_v}{G^3}+\frac{\Gamma_b \delta D_b}{G^4}\right), \tag{1}$$

where γ is the surface energy, Ω is the atomic volume, k is the Boltzmann constant, T is the absolute temperature, G is the mean grain size, t is the time, L is the sample length, D_v is the coefficient of volume diffusion, D_b is the coefficient of grain boundary diffusion, δ is the thickness of grain boundary and Γ represents geometric factors as the driving force in sintering.

To evolve MSC the following assumptions have been made - the shrinkage is isotropic and the sintering process is governed only by a single dominating mechanism [1]:

$$\frac{k}{\gamma\Omega\delta D_0}\int_{\rho_0}^{\rho}\frac{(G(\rho))^n}{3\rho\Gamma(\rho)}d\rho=\int_0^t\frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt \tag{2}$$

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As it can be seen, there are only microstructure variables (grain size G and density ρ) on the left side of Eq. (2), while the right side of Eq. (2), usually denoted as

$$\Theta(t,T(t)) \equiv \int_0^t \frac{1}{T}\exp\left(-\frac{Q}{RT}\right)dt\,, \tag{3}$$

presents the thermal history of the sintering process. If we are able to find one single activation energy Q for which the functions

$$\rho_i = f(\Theta_i) \tag{4}$$

(where Θ_i are the thermal histories of different sintering heating profiles) are overlapping, we have found the so-called MSC. In such a case the grain size is independent of thermal history and it is only a function of density (of course, the same powder compacts have to be used for all experiments). This fact was confirmed for many ceramics [3-10] and metal powder compacts [10,11] during the last 30 years. Using the concept of MSC the density evolution of a given powder compact at different heating schedules can also be predicted.

Unfortunately, the calculation of dependences $\rho_i = f(\Theta_i)$ needs repeated numerical calculations which are user-unfriendly. In this work we present simple software which significantly simplifies the calculation of MSC. Additionally, we compare the commonly used criterion of overlap of $\rho_i = f(\Theta_i)$ curves (Mean Residual Squares, MRS in the following) with our newly proposed criterion (called Mean Perpendicular Curves Distance, MPCD in the following). The advantages of our approach are demonstrated by evaluating the sintering of two different alumina- and two different zirconia-powder compacts.

2. Criteria of $\rho_i = f(\Theta_i)$ curves overlap

The standard statistical approach to evaluating the scatter of experimental data is the minimization of MRS. This criterion was used in many recent papers [1,5,12,13] to determine the sintering activation energy and construction of MSC and is described, for example, in [12] by the following formula:

$$MRS = \sqrt{\frac{1}{\rho_f - \rho_0}\int_{\rho_0}^{\rho_f}\frac{\sum_{i=1}^{N}\left(\left(\Theta_i / \Theta_{avg}\right)-1\right)^2}{N}d\rho}\,, \tag{5}$$

where Θ_{avg} is the average of all Θ_i at a given density, N is the number of heating profiles used, and ρ_0 or ρ_f are green or final densities of the sample.

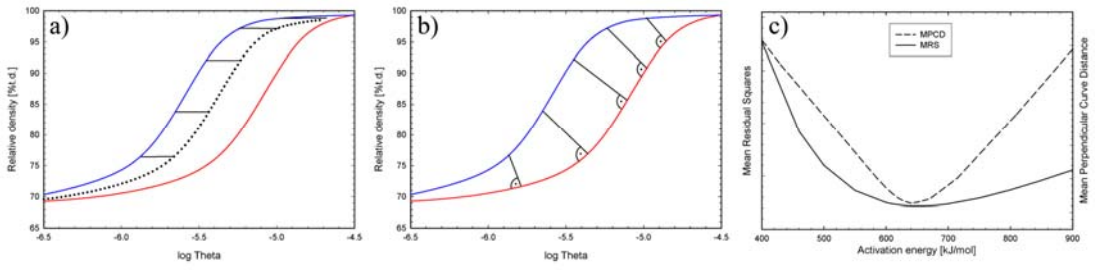

Fig. 1. Criteria for determination of overlap of individual MSCs: a) Mean Residual Squares; b)Mean Perpendicular Curve Distance; c) Comparison of both methods

Taking into account the sigmoid shape of MSC we can expect that distance of curves can be overestimated in the first and final sintering stages (Fig. 1a). Therefore we have developed an alternative method (MPCD) for evaluating the overlap of $\rho_i = f(\Theta_i)$ curves. In

the MPCD method we follow Eq. 6

$$\mathrm{MPCD} = \int_{\rho_0}^{\rho_f} \frac{\sum_{i=1}^{N} PD_i(\rho)}{\rho_f - \rho_0} d\rho \,, \tag{6}$$

where the perpendicular distance (PD) of individual curves is evaluated (Fig. 1b) instead of horizontal ones (Fig. 1a).

Fig. 1c shows a typical dependence of MRS and MPCD on the chosen activation energy of the same sample. The activation energy of sintering process is given by the minimum of MRS or MPCD. It can be seen that the dependence is flatter for the MRS criterion and therefore the activation energy can be evaluated more precisely using the MPCD criterion.

3. Software for calculation of MSC

Since all calculations associated with MSC are complicated and time-consuming, we have developed an automatic procedure simplifying the construction of MSC. The software can import (in the xls, asc or txt formats) up to 10 different densification curves (Fig. 2a). Then the dependence of MPCD (or MRS) on activation energy is calculated (Fig. 2b). The user can refine the scale and find the activation energy more precisely. Finally the best overlap of the curves is shown and data are exported again in the xls, asc or txt format (Fig. 2c).

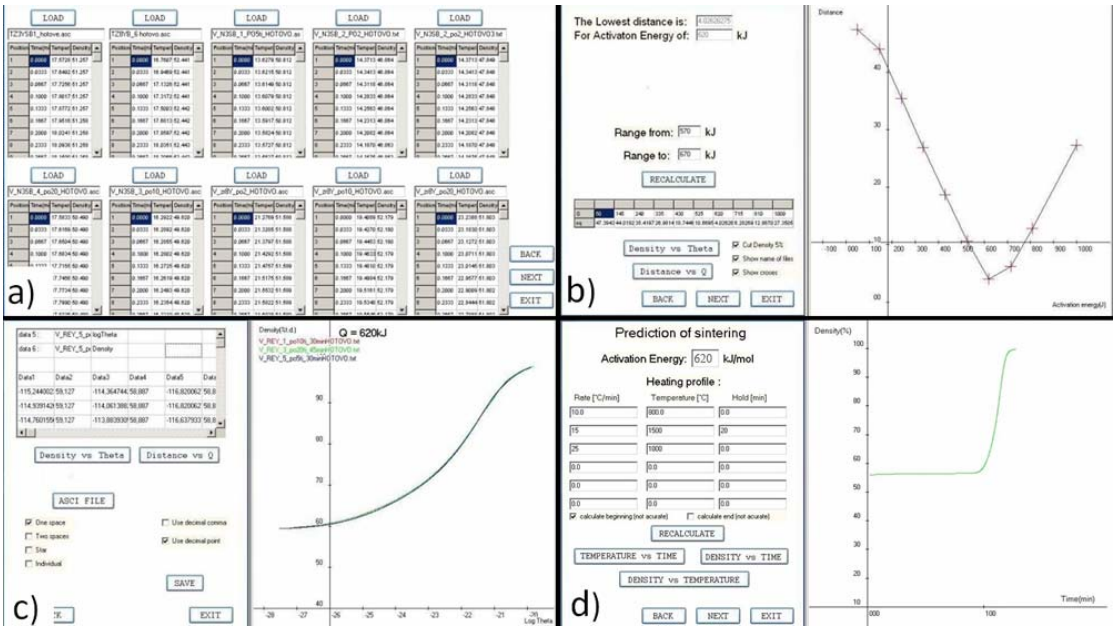

Fig. 2. Steps of calculation of MSC: a) Import of data; b) The dependence of MPCD (or MRS) on activation energy; c)The best overlap of MSCs and export of data; d) The prediction via MSC concept

Once the activation energy and the shape of MSC are known, we can predict the densification of the given sample for any sintering profile. Since it is only a problem of

numerical calculation of Eq. (2), the software enables also this option (Fig. 2d). The software is freely available for the research community and can be requested via email to authors.

4. Experimental

Materials

Four types of commercially available ceramic powders were used. The details of these powders are given in Tab. I. The particle size D_{BET} was calculated from a specific surface area established by nitrogen absorption (BET method, ChemBet 3000, Quantachrome, USA). The following values of theoretical densities were used for the calculation of average particle size from the specific surface area (as well as in further text for the calculation of relative densities): $\rho_{th}(TAI) = \rho_{th}(REY) = 3.99 g \cdot cm^{-3}$; $\rho_{th}(Z3Y) = 6.08 g \cdot cm^{-3}$; $\rho_{th}(Z8Y) = 5.99 g \cdot cm^{-3}$.

Tab. I BET particle size of ceramic powders used

Powder	Producer	Grade	Abbreviation	D_{BET} [nm]
Al_2O_3	Taimei Chemicals, Japan	Taimicron TM-DAR	TAI	100
Al_2O_3	Malakoff Industries, USA	RC-HP DBM	REY	240
ZrO_2 (+3mol%Y_2O_3)	Tosoh Corporation, Japan	TZ-3YSB	Z3Y	140*
ZrO_2 (+8mol%Y_2O_3)	Tosoh Corporation, Japan	TZ-8YSB	Z8Y	140*

* values of specific surface area given by the producer

Preparation of Ceramic Green Bodies

Disks of 30 mm in diameter and ca. 5 mm in height were prepared from the above materials, via cold isostatic pressing (CIP). Pressing was carried out in an isostatic press (Autoclave Engineering, Inc., USA) at a pressure of 300 MPa with a dwell time of 5 minutes. The CIPed samples were presintered at 800°C/1h, then cut and ground in the shape of prisms of ca. 4x4x15mm for sintering in the dilatometer.

Sintering of ceramic bodies

The samples were sintered in a high-temperature dilatometer (L70/1700, Linseis, Germany) in air atmosphere. Sintering shrinkage curves were recalculated to the densification profiles. The details of such recalculation are described elsewhere [14]. The final relative densities of samples (ρ_{rel}) were determined on the basis of Archimedes' principle (EN 623-2) with distilled water and using the above-mentioned theoretical densities.

5. Results and discussion

Construction of MSC

The master sintering curve was calculated for all four materials with all heating rates given in Tab. II. The minimum distance of curves ρ=f(Θ) was calculated using the two criteria mentioned. Figs 3a,c,e,g show the influence of MPCD and MRS on a selected activation energy. All graphs contain only one minimum; in all cases this minimum was deeper for the MPCD criterion. An overview of all the calculated activation energies is given in Tab. III, and MSCs constructed with these activation energies are plotted in Figs 3b,d,f,h. This paper should only demonstrate the possibility of quickly and precisely constructing the MSC. A detailed discussion of activation energies obtained in this work will be given in a follow-up paper.

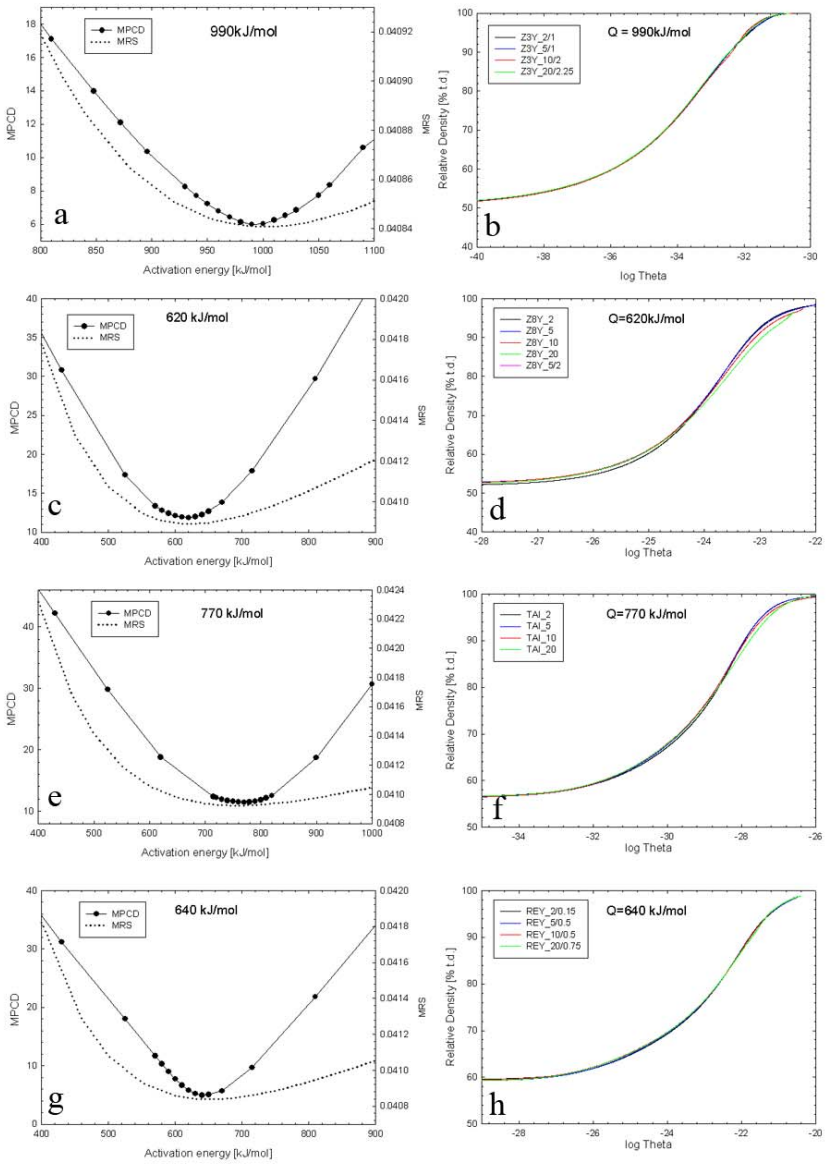

Fig. 3. The dependence of MPCD on activation energy and the overlap of MSCs for a,b) Z3Y, c,d) Z8Y, e,f) TAI, g,h) REY

Tab. II. Sintering schedules and reached densities

Sample name	Heating rate [°C/min]	Dwell on temperature [°C/h]	ρ_{rel} [%]	s/n [%/-]
Z3Y_2/1	2	1500/1	99.73	0.06/9
Z3Y _5/1	5	1500/1	99.75	0.06/9
Z3Y _10/2	10	1500/2	100.01	0.08/9
Z3Y _20/2.25	20	1500/2.25	100.16	0.14/9
Z8Y_2	2	1500/0	98.81	0.07/9
Z8Y _5	5	1500/0	98.08	0.05/9
Z8Y _10	10	1500/0	97.27	0.07/9
Z8Y _20	20	1500/0	96.41	0.08/9
Z8Y _5/2	5	1450/2	99.25	0.06/9
TAI_2	2	1500/0	99.67	0.07/9
TAI _5	5	1500/0	99.63	0.10/9
TAI _10	10	1500/0	99.59	0.10/9
TAI _20	20	1500/0	99.59	0.14/9
REY_2/0.15	2	1500/0.15	98.09	0.08/9
REY _5/0.5	5	1500/0.50	98.46	0.05/9
REY _10/0.5	10	1500/0.50	98.41	0.03/9
REY _20/0.75	20	1500/0.75	98.80	0.06/9

Note: s is standard deviation, n is number of measurement

Tab. III. Sintering activation energies calculated by different criterions

Powder	Criterion	Z3Y	Z8Y	TAI	REY
Activation energy	MPCD	990	620	770	640
[kJ/mol]	MRS	1000	620	760	650

Prediction via MSC concept

Knowing the value of activation energy and shape of MSC for a given powder compact, it should be possible to predict its densification behavior. This possibility was tested with TAI alumina green bodies, which were sintered at a constant heating rate (10°C/min) to three different dwell temperatures. Tab. IV shows the comparison of predicted and actually obtained final densities while Fig. 4 represents the good agreement of predicted densification profiles with the actual ones.

Tab. IV. The comparison of predicted and really reached final densities of TAI samples sintered at three different temperatures and dwell times

Sample name	Type	Temperature [°C]	Dwell [min]	ρ_{rel} [%]
1350/120_A	prediction	1350	120	99.50
1350/120_B	experimental	1350	120	99.62
14000/46_A	prediction	1400	46	99.60
14000/46_B	experimental	1400	46	99.64
1450/8_A	prediction	1450	8	99.60
1450/8_B	experimental	1450	8	99.58

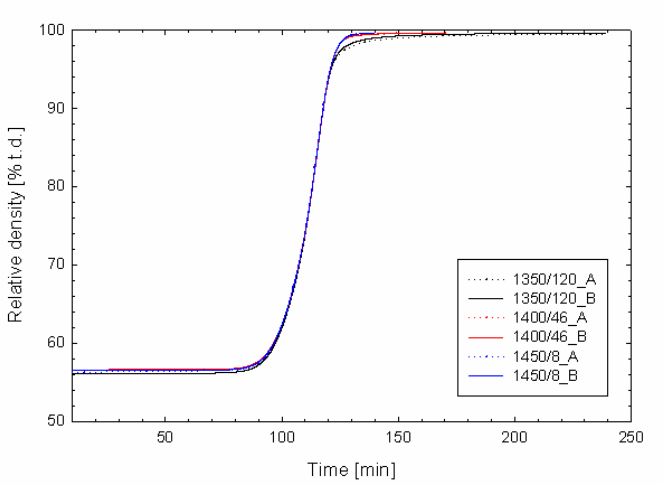

Fig. 4. Prediction and experimental verification of densification profiles of TAI alumina samples

6. Conclusion

A practical method for the construction of MSC is presented in the paper. With the help of a few dilatometric sintering experiments the newly developed software calculates MSC and finds the optimal activation energy of a given material. The method was verified on cubic and tetragonal zirconia powder compacts and on two alumina powder compacts of different particle sizes. Also the possibility of predicting the sintering behaviour via MSC concept was presented.

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Садржај: *Концепт мастер криве синтеровања представља добро оруђе sa оптимизацију процеса синтеровања. Међутим, конструкција мастер криве из података о синтеровању укључује компликован и дуготрајан рачун. У овом раду дата је практична метода за конструкцију мастер криве синтеровања. Развијени софтвер рачуна мастер криву на основу неколико експеримената синеровања у дилатометру и налази оптималну енергију активације за дати материјал. Софтвер, који такође омогућује предвиђање синтеровања је верификован синнтеровањем кубичног цирконијума и алумине са две различите величине честица.*

Кључне речи: *Алумина, цирконијум, мастер крива синтеровања, предвиђање згушњавања.*