



Master sintering curves of two different alumina powder compacts[#]

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Abstract

Concept of Master Sintering Curve is a strong tool for optimizing sintering schedule. The sintering behaviour can be predicted, and sintering activation energy can be calculated with the help of few dilatometric measurements. In this paper an automatic procedure was used to calculate Master Sintering Curves of two different alumina compacts. The sintering activation energies were determined as 640 kJ/mol for alumina with particle size of 240 nm, respective 770 kJ/mol for alumina with particle size of 110 nm. The possibility to predict sintering behaviour with the help of Master Sintering Curve was verified.

Keywords: alumina, sintering, Master Sintering Curve

I. Introduction

Sintering is a very complicated process of microstructure evolution. This evolution is thermally activated process with development of bonds among particles via moving of atoms and ions. Since sintered materials are not melted, all movements are realized via diffusion process.

Concept of Master Sintering Curve (MSC) comes from physical sintering models derived by Johnson and coworkers [1,2]. It is expressed by the following equation:

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

where γ is the surface energy, Ω is the atomic volume, k is the Boltzmann constant, T is the thermodynamic temperature, G is the mean grain size, ρ is sample density, D_0 is the coefficient of diffusion process (only one dominant diffusion process is expected), Q is the sintering activation energy, Γ represents geometric factors and driving force for sintering, and t is the time.

In this equation, there are separated parameters describing microstructural evolution (left side of the equa-

tion) from parameters describing thermal history (right side of the equation). The right side of equation (1) is usually assigned as:

$$\Theta(t, T(t)) \equiv \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (2)$$

Activation energy Q can be calculated with the use of few densification curves with different heating schedules. The true activation energy is that for which functions

$$\rho = f(\Theta) \quad (3)$$

are overlapping for all tested heating profiles. As soon as the activation energy of given sample is known, the prediction of densification of the sample subjected to various heating schedules is possible. The main objective of this paper is the construction of MSCs of two alumina compacts with different particle size, and calculation of their activation energies. The second goal of this work is to verify the possibility to predict sintering behaviour with the help of MSC [3,4].

II. Experimental

Materials

Two types of commercially available α -alumina ceramic powders were used. The details of these powders are given in Table 1. The particle size D_{BET} was calculated from specific surface area (SSA) established by nitrogen absorption (BET method, ChemBet

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Table 1. Details of ceramic powders used

Material	Producer	Grade	Abbreviation	SSA [m ² /g]	D _{BET} [nm]
α-Al ₂ O ₃	Taime Chemicals, Japan	Taimicron TM-DAR	TAI	15.1	100
α-Al ₂ O ₃	Reynolds Chemicals, USA	RC-HP DBM	REY	6.3	240

Table 2. Sintering schedules and reached final relative densities

Sample name	Heating rate [°C/min]	dwelt [°C/min]	ρ _{rel} [%]	s/n* [%/-]
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
TAI_1400/46**	10	1400/46	99.64	0.06/9
REY_2/0.15	2	1500/15	98.09	0.08/9
REY_5/0.5	5	1500/30	98.46	0.05/9
REY_10/0.5	10	1500/30	98.41	0.03/9
REY_20/0.75	20	1500/45	98.80	0.06/9

* *s* is standard deviation, *n* is number of measurements

** This sample was not used for calculation of activation energy, it served for verification of densification prediction

3000, Quantachrome, USA) with assumption of unimodal spherical particles and alumina theoretical density 3.99 g cm⁻³.

Preparation of ceramic green bodies

Disks of 30 mm in diameter and about 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, than cut and ground into the shape of prisms of 4×4×15 mm.

Sintering of ceramic bodies

The samples were sintered in high-temperature dilatometer (L70/1700, Linseis, Germany) in air atmo-

sphere. Sintering shrinkage curves were recalculated to the densification profiles. The details of such recalculation are described elsewhere [5].

Relative densities of sintered samples

The final relative densities of samples (ρ_{rel}) were determined on the basis of Archimedes' principle (EN 623-2) with distilled water as a liquid media and using above mentioned theoretical density.

Calculation of MSC

Construction of MSC (calculation of activation energy as well as densification prediction) was provided by software Density MSC [6]. Mean perpendicular curve distance [6] was used as a criterion for finding optimal activation energy of sintering process.

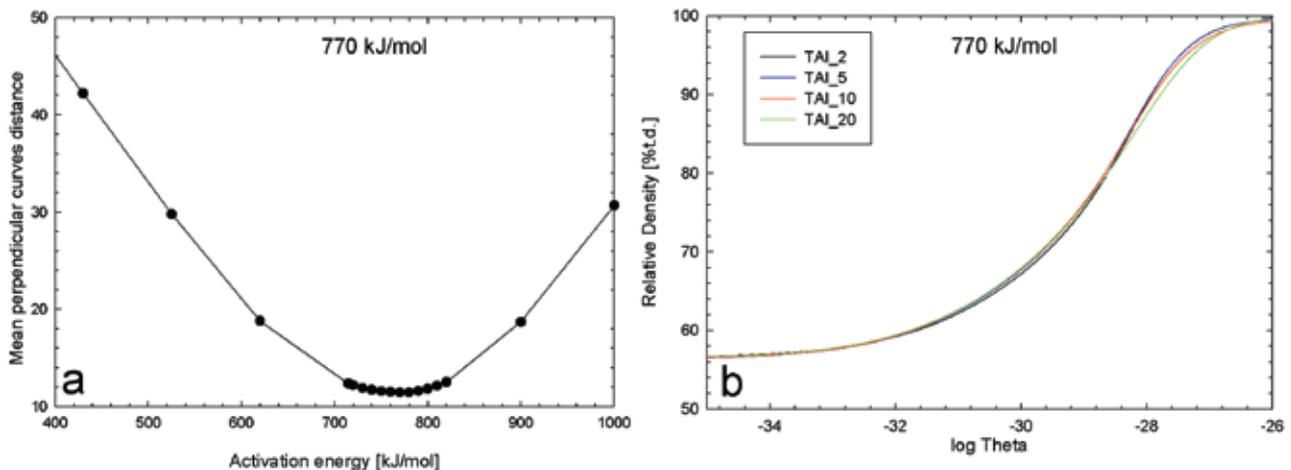


Figure 1. Calculation of activation energy via MSC method for TAI (a) and MSC for TAI (b) (true activation energy is 770 kJ/mol)

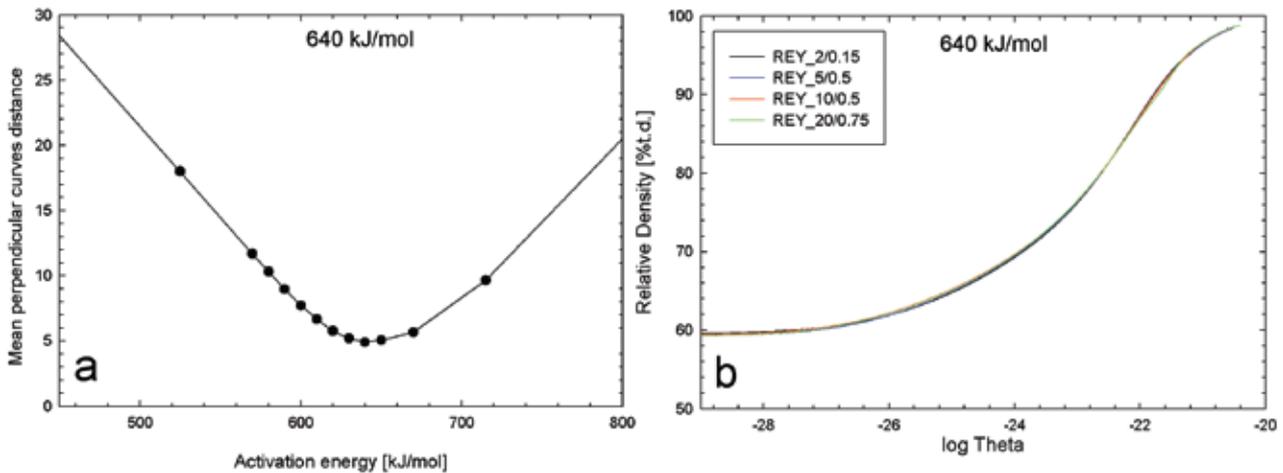


Figure 2. Calculation of activation energy via MSC method for REY (a) and MSC for REY (b) (true activation energy is 640kJ/mol)

III. Results and discussion

MSC was calculated from four different heating profiles (differing by heating rates 2, 5, 10, 20°C/min) for both alumina compacts. All heating profiles as well as reached final relative densities are summarized in Table 2.

Fig. 1a shows the dependence of mean perpendicular curves distance (which reflects quality of the overlap of MSCs belonging to all four heating rates) in dependence on chosen activation energy for material TAI. This dependence has only one minimum at $Q = 770$ kJ/mol. Very good overlap of MSCs calculated with this value of activation energy (see Fig. 1b) indicates that 770 kJ/mol can be considered as true activation energy for this sample. Similar behaviour had REY alumina sample (see Fig. 2a,b) but the optimal activation energy was evaluated as 640 kJ/mol.

The results showed that sintering activation energy is not only a function of material composition. Our samples were prepared from powders differing by particle size (100 nm for TAI, 240 nm for REY). At the moment we do not have any evidence that particle size itself is the reason for different sintering activation energies but

we assume that the reason is more likely in different green body microstructure (different particle shape and size, as well as different pore size, shape and distribution). Big scatter of values of sintering activation energies reported in the literature for alumina (342 kJ/mol [7], 384 kJ/mol [7], 480 kJ/mol [1], 1064 kJ/mol [3], 496 – 1000 kJ/mol in dependence on heating rate [8]) supports this hypothesis.

Based on activation energy of sintering process obtained for TAI sample, the densification of this material was predicted with the help of MSC concept [5] for the sintering with heating rate of 10°C/min and 1400°C with a dwell time of 46 minutes. Overlap of numerically predicted and experimentally assigned evolution of density is given in Fig. 3. Agreement between predicted and experimental values of density was within the range of standard deviation of density measurement (0.06% t.d.) during whole sintering process. From this point of view the concept of MSC looks as a strong and useful tool how to design sintering process.

IV. Conclusions

Sintering activation energy of two different alumina compacts was evaluated via concept of MSC. The calculated activation energies were 770 kJ/mol for alumina with particle size of 110 nm, respective 640 kJ/mol for alumina with particle size of 240 nm. The possibility to predict sintering behaviour with the help of MSC was tested by sintering at a heating rate of 10°C/min and 46 min dwell at 1400°C. Agreement of predicted data and experimental data of density during whole sintering cycle shows validity of established activation energy and demonstrates high application potential of MSC concept.

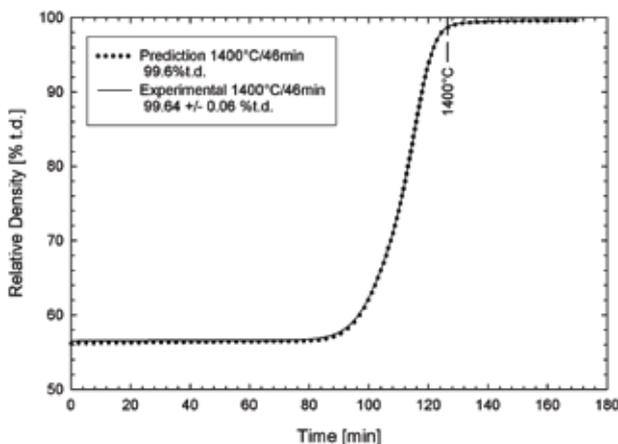


Figure 3. Overlap of predicted and measured densities of TAI sample after sintering at 1400°C/46min

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