



## A critique of master sintering curve analysis

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### ABSTRACT

In this work, we explore factors affecting the accuracy of the master sintering curve (MSC) approach for analyzing the complete sintering profile of ceramic powders. We show that the instantaneous anisotropic shrinkage must be accounted for to develop an accurate MSC. The MSC diverges at > 90% density because of basic assumptions that oversimplify the analysis of the densification process. We also show that powder chemistry and forming techniques can affect the fitting parameter  $Q$ .  $Q$  should not be interpreted as the sintering activation energy, or used to interpret mechanistic differences since it is comprised of several mechanisms that influence densification throughout the sintering cycle. Despite these limitations, the MSC is a useful and practical tool for predicting thermal load (i.e. time and temperature) effects on the densification of a ceramic part fabricated from a singular powder that is fabricated by a singular forming process.

### 1. Introduction

The master sintering curve (MSC) approach was developed by Su and Johnson [1] to generalize the densification behavior of a sintering powder with a single curve for the entire sintering time/temperature profile. The MSC approach is based on a combined-stage sintering model developed by Hansen et al. [2], given as:

$$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{3\gamma\Omega}{k_B T} \left( \frac{\delta D_b \Gamma_b}{G^4} + \frac{D_v \Gamma_v}{G^3} \right) \quad (1)$$

where  $\rho$  is relative density of the powder compact,  $d\rho/dt$  is densification rate,  $\gamma$  is surface energy,  $\Omega$  is molar volume,  $k_B$  is Boltzmann's constant,  $T$  is absolute temperature,  $G$  is grain size,  $D$  is diffusion coefficient,  $\delta$  is grain boundary thickness, and  $\Gamma$  is a geometric scaling factor. The subscripts  $b$  and  $v$  represent grain boundary and volume diffusion mechanisms, respectively. The MSC was originally derived to simplify the combined-stage sintering model (Eq. 1) to account for only a single diffusion mechanism, and by considering diffusion as thermally-activated with an activation energy  $Q$ . The resulting equation is given as:

$$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{3\gamma\Omega}{k_B T} \left( \frac{D\Gamma}{G^n} \right) \quad (2)$$

where

$$D = D_0 e^{-Q/RT} \quad (3)$$

and  $R$  is the ideal gas constant. Eq. (2) is re-written to collect

microstructural parameters on the left hand side and temperature dependent parameters on the right hand side:

$$\frac{k_B G^n}{3\gamma\Omega\Gamma D_0} \frac{d\rho}{dt} = \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) = \frac{d\Theta}{dt} \quad (4)$$

Eq. 4 can be integrated to give:

$$\frac{k_B}{\gamma\Omega D_0} \int_{\rho_0}^{\rho} \frac{(G(\rho))^n}{3\rho\Gamma(\rho)} d\rho = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt = \Theta \quad (5)$$

Eq. (5) describes the sintering behavior for an arbitrary time-temperature profile, and the integral over this profile with respect to time is termed the work of sintering  $\Theta$ . The MSC is obtained by plotting  $\rho$  versus  $\Theta$ . The left hand side of Eq. (4) is not solved, because many of the parameters are unknown. However, as long as these parameters are independent of time and temperature, data plotted in this way will collapse into a single continuous curve for a single value of  $Q$ . It is interesting to note that the MSC analysis is independent of the sintering mechanism and, as a generalized model, was applied to other thermally activated process such as grain growth [3] and binder decomposition [4,5].

In practice,  $Q$  is a fitting parameter for which the best-fit MSC is obtained over a range of heating rates by determining the minimum mean residual. Assuming arbitrary values for  $Q$  in Eq. (5), the mean residual square is calculated by [6]

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**Table 1**  
Q values obtained by MSC analysis for different alumina powders.

Alumina grade	Forming technique	Heating rates (°C/min)	Q (kJ/mol)	Ref.
AKP-50 Sumitomo Chemicals	CIP (270 MPa)	60 to 750 °C 8–45 to 1500 °C	440	[1]
AKP-50 Sumitomo Chemicals	Uniaxial pressing (50 MPa) CIP (200 MPa)	3–20 to 1400 °C	555	[7]
AKP-50 + 2000 ppm MgO Sumitomo Chemicals	Uniaxial pressing (50 MPa) CIP (200 MPa)	3–20 to 1400 °C	880	[7]
Taimicron TM-DAR Taimai Chemicals	CIP (300 MPa)	2–20 to 1500 °C	770	[8]
RC-HP DBM Reynolds Chemicals	CIP (300 MPa)	2–20 to 1500 °C	640	[8]
Taimicron TM-DAR Taimai Chemicals	Uniaxial pressing (50 MPa) CIP (200 MPa)	2–25 to 1400 °C	700	[9]
Taimicron TM-DAR Taimai Chemicals	Pressure filtration (40 MPa)	2–25 to 1400 °C	605	[9]
Taimicron TM-DAR Taimai Chemicals	SPS (50 MPa)	35–150 to 1200 °C	290	[10]
99.9%, Dalian Luming Nanometer Materials	Uniaxial pressing (80 MPa) CIP (250 MPa)	0.5–5 to 1640 °C	1064	[11]

$$\text{Mean residual square} = \sqrt{\frac{1}{\rho_S - \rho_0} \int_{\rho_0}^{\rho_S} \frac{\sum_{i=1}^N \left( \frac{\Theta_i}{\Theta_{avg}} - 1 \right)^2}{N} d\rho} \quad (6)$$

where N is the number of experimental data points gathered at a series of heating rates and a sintered density  $\rho_S$ , and  $Q_{avg}$  is the average of all  $Q_i$  over N. The Q value that yields the minimum mean residual square is the Q value at which the MSC trajectories obtained from the densification curves at different heating rates yield the best fit and converge onto a single curve. Because of the mechanistic nature of the model, the Q parameter is usually referred to in the literature as the ‘activation energy’ for sintering.

MSC analysis has been applied to ceramic powders formed and densified by a variety of techniques. For high purity alumina, the reported Q values vary drastically, as seen in Table 1. In Su and Johnson’s original work, [1] Q values of 440 and 488 kJ/mol were determined by minimum mean residuals and iso-strain analysis, respectively, for an ultrafine, ultrahigh purity alumina (AKP-50, Sumitomo Chemical America, Inc.), showing that the activation energy obtained from minimum mean residuals is in close agreement with the activation energies determined by conventionally used methods. Using the same powder, Tatami et al. [7] determined a Q of 555 kJ/mol, and when the powder was doped with 2000 ppm MgO, a Q of 880 kJ/mol was determined. Pouchly et al. estimated the Q of two different ultrahigh purity alumina powder graded (Taimicron TM-DAR, Taimai Chemicals and RC-HP DBM, Reynolds Chemicals) to be 770 and 640 kJ/mol, respectively, and attributed the difference in Q to the difference in particle size of 110 nm and 240 nm, respectively. Aminzare et al. [8] reported Q values of 700 and 605 kJ/mol for alumina (Taimicron TM-DAR, Taimai Chemicals) samples prepared by dry pressing and pressure filtration, respectively. Using the same alumina powder grade (Taimicron TM-DAR, Taimai Chemicals), Guillon and Langer [10] reported a Q of 290 kJ/mol for  $Al_2O_3$  densified by spark plasma sintering (SPS). They attributed the lower Q value to the effect of the high heating rates of 35 – 150 °C/min during SPS. Q values of up to 1064 kJ/mol were reported by Shao et al. [11] for granulated and dry pressed alumina powder (350 nm, 99.9%, Dalian Luming Nanometer Material Ltd.). They explained the higher Q values as an effect of slower heating rates (0.5 and 5 °C/min) on densification.

The effect of heating rate on densification was explained by Harmer and Brook [12] as due to the relative time the material is heated under conditions favoring surface and grain boundary diffusion. They reasoned that a slow heating process favors surface diffusion and particle coarsening because surface diffusion usually has a lower activation energy than densification mechanisms such as grain boundary and volume diffusion. Samples heated at slow rates spend relatively longer times at lower temperatures and, therefore, experience more particle coarsening prior to reaching the temperatures where densification occurs. Thus, the driving force for sintering provided by surface area is higher during the densification stage when ceramics are fired at higher heating rates since these samples do not undergo as much coarsening prior to densification. In MSC analysis, these relative changes in mechanism result in lower Q values at faster heating rates. However, it is assumed in the MSC analysis that sintering occurs by a single mechanism for the heating conditions used to collect densification data. Since data for MSC analysis is performed by heating samples at different heating rates, the contributions from surface diffusion and grain boundary diffusion vary, and it is questionable if the Q values obtained can be used for mechanistic interpretations. Furthermore, it is not apparent what other parameters, in addition to the heating rate, cause the large variability of the reported Q values.

In this work we investigate how forming techniques and powder chemistry affect the Q parameter and the shape of the MSC for a commercial specialty alumina powder. We explore how forming process-induced differences in relative green density, microstructural homogeneity and shrinkage anisotropy affect the value of Q. We also

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