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Master Sintering Surface – A Practical Approach to Its Construction and Utilization for Spark Plasma Sintering Prediction

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Abstract:

The sintering is a complex thermally activated process, thus any prediction of sintering behaviour is very welcome not only for industrial purposes. Presented paper shows the possibility of densification prediction based on concept of Master Sintering Surface (MSS) for pressure assisted Spark Plasma Sintering (SPS). User friendly software for evaluation of the MSS is presented. The concept was used for densification prediction of alumina ceramics sintered by SPS.

Keywords*: Spark Plasma Sintering, Master Sintering Surface, Sintering kinetics, Alumina*

1. Introduction

The sintering of ceramics always leads to reduction of sample size. The sintering shrinkage in conventional materials is typically between 12 and 25% of the relative length of sample, thus it is easy to measure it [1]. Three variables can be simultaneously recorded in a high-temperature dilatometer: time, temperature and length of the sample. The change of sample length itself consists of sum of the following changes: temperature expansion of the sample [2], phase transformations [3] and sintering shrinkage [4]. If sintering shrinkage can be separated, then it is possible to recalculate the sintering shrinkage to a densification curve. Such recalculation is described in our previous paper [5]. Once the densification curve is created, one can simply follow the heating profile and stop sintering at a required density. This can be beneficial for easy finding the temperature for first step of Two-Step Sintering [6, 7] or the temperature necessary for closed porosity for post-HIPing [8]. The problem occurs, when the different heating rate, sintering temperature or dwell time is desirable.

This problem can be overcome via Master Sintering Curve (MSC) concept. The MSC was derived by Su and Johnson in 1996 [9] from simplified sintering model published by Hansen and co-workers [10]:

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

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where L is the sample length, t is the time, 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, 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. If a single diffusion mechanism is responsible for densification and, at the same time, the microstructure is function only of sample density (so it is independent of thermal history), we can rearrange Eq. (1) to Eq. (2):

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

where Q is the apparent activation energy of sintering process, R is the gas constant and ρ is density. If the right side of this equation is denoted as Θ, the relationship between ρ and Θ is entitled as MSC [9]. The usual construction of MSC is carried out via few constant heating rate experiments followed by optimization of activation energy value to achieve best overlap among individual $\rho=f(\Theta)$ functions [11]. If such activation energy is found, $\rho=f(\Theta)$ functions for all experiments become one (master) curve [12].The obtained MSC together with Eq.(2) can be used for prediction of densification curve of any heating schedule of the same ceramic green body [13].

An and Han [14] accommodated MSC to pressure-assisted sintering by introducing another independent variable – pressure; they constructed so-called Master Sintering Surface (MSS). The applied pressure generally shifts the densification curve to lower temperatures. This improved model enables also densification prediction with variations in: heating rate, sintering temperature, dwell time and pressure. The calculations, which lead to MSS construction, are complicated and time-consuming. To bridge this problem we developed simple and user-friendly software for MSS construction.

The Spark Plasma Sintering (SPS) is very promising technique for sintering of ceramics, metals, composites etc. In SPS the pulsed DC powder is combined with an applied pressure for the purpose to enhance sintering process. Pulsed Joule heat provides the advantage of rapid temperature increase (up to several hundred °C/min) and possibility to electro- migration or electro-plasticity [15]. If the sample is not conductive (as alumina in this paper) the passing current heats the die and material is heated due to convection of heat. The SPS can usually record the motion of pressing ram during the sintering process. The SPS thus can work as a simple high temperature and pressure dilatometer, which allows construction of MSS from SPS experiments.

The main goal of this paper is to describe the easy way of construction of MSS and to show its utilization for SPS description and prediction in case of alumina ceramics.

Software for calculations of MSS

The software can import (in the xls, asc or txt format) up to 10 different densification curves with different heating rates, sintering temperatures, dwells, and pressure values. Then the dependence of Mean Perpendicular Curve Distance (MPCD) [16] or Mean Residual Squares (MRS) is used to find the optimal activation energy and to develop the MSS of used ceramic material (see Fig. 1). With this MSS, the software can predict densification behaviour of given sample for any temperature-pressure sintering profile. The export of MSS calculations is possible in xls, asc, or txt format. All the steps can be done automatically or manually. The software is available for research community for free and can be requested via email to authors.

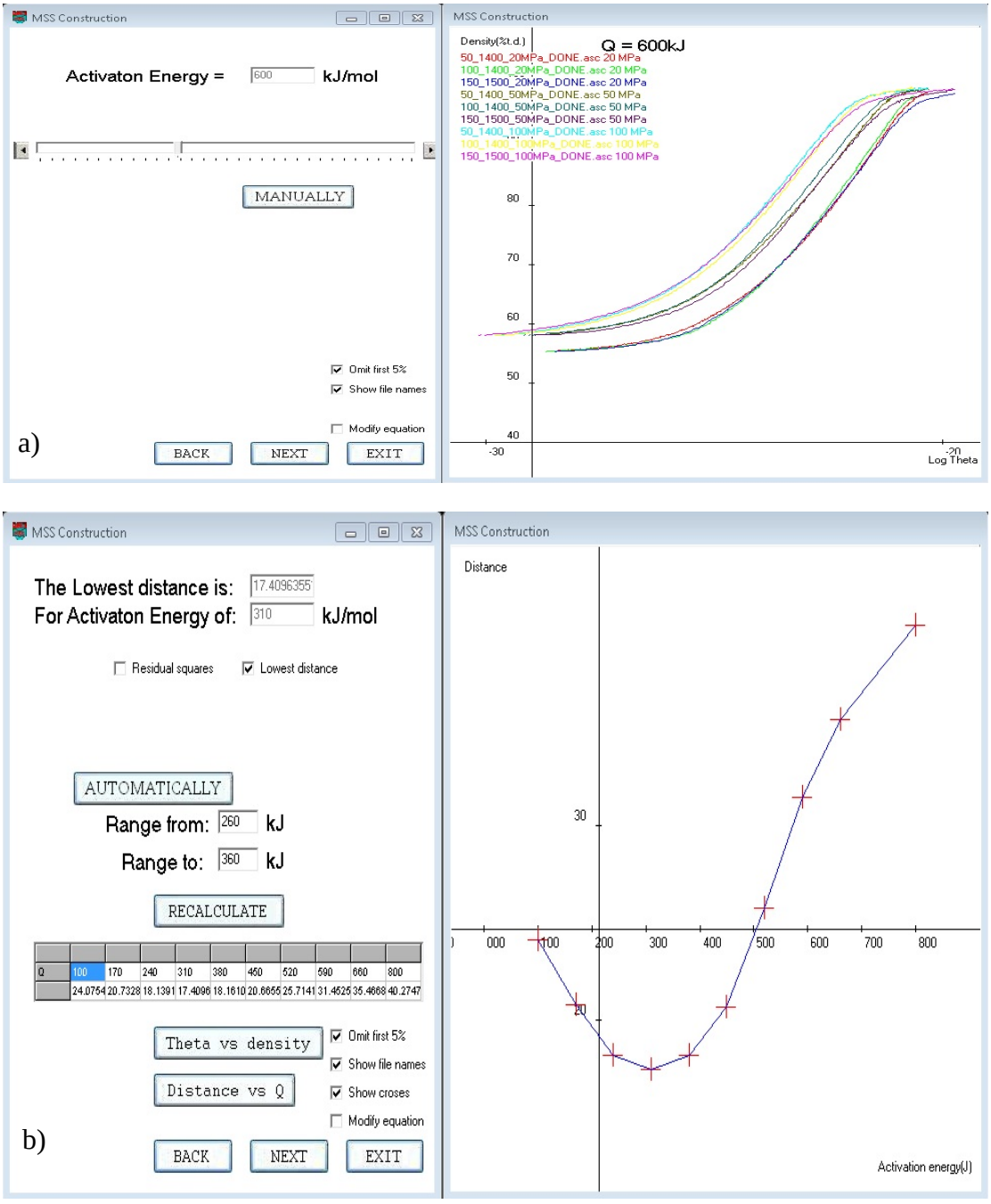


Fig. 1. Print screen from the software a) Individual $\rho=f(\Theta)$ functions, b) Establishing of optimal activation energy

2. Experimental

To verify presented concept of MSS, the SPS experiments with alumina powder AKP 30 (Sumitomo Chemical America Inc. New York, median particle size 300 nm) were performed. Sintering as well as shaping was provided in SPS Dr. Sinter 2050 (Sumitomo Coal Mining Co., Japan) apparatus. The 2.3g of powder was loaded into a graphite die with inner diameter of 12 mm. The outer surface of the die was covered by graphite blanket with a

thickness of ~7 mm to minimize the heat loss and to improve temperature distribution during sintering. The temperature was measured using optical pyrometer focused on a small hole drilled into a surface of a die. The pressure was raised on its final value during preheating up to 600°C, and then held constant during whole sintering process. The initial densities of samples for SPS were measured geometrically with precision of ±2% of theoretical density (t.d.).

The MSS was constructed from three independent MSCs. Four heating rates 50, 100, 150 and 200 °C/min and pressures of 20, 50 and 100MPa were used for construction of individual MSCs. Every individual MSC was created for a different value of pressure. MPCD was used to find optimal activation energy. All MSCs were than combined into a MSS. Final relative densities were determined on the basis of the Archimedes principle (EN 623-2) with distilled water and using alumina t.d. of 3.99g/cm^3.

3. Results and discussion

All of the heating schedules and reached final densities are summarized in Tab. I. The lowest value of final density (97.08%t.d.) had the sample 200/1400/20 (heating rate 200°C/min, final temperature 1400°C without dwell, applied pressure of 20MPa) . This result was expected according to basic sintering theory; nevertheless also small final relative density would allow usage of the MSC concept.

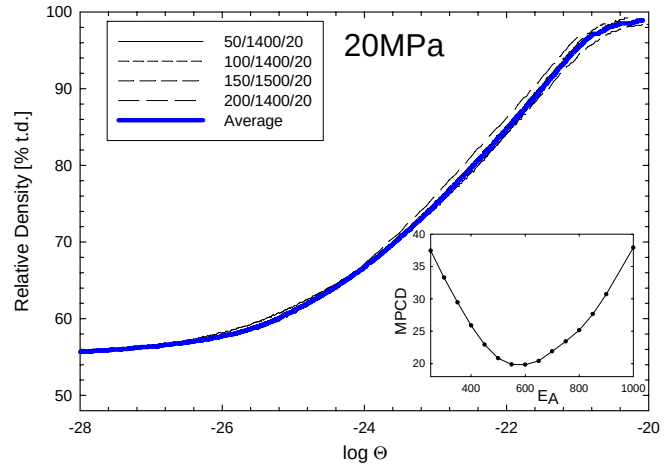
Tab. I List of all used heating schedules and obtain densities

Abbreviation	Heating rate [°C/min]	Target temperature [°C]	Holding time [min]	Pressure [MPa]	Final density [%t.d.]	s/n [%/-]
50/1400/20	50	1400	0	20	99.22	0.06
100/1400/20	100	1400	0	20	98.46	0.03
150/1400/20	150	1500	0	20	98.90	0.04
200/1400/20	200	1400	0	20	97.08	0.02
50/1400/50	50	1400	0	50	99.61	0.04
100/1400/50	100	1400	0	50	99.49	0.02
150/1400/50	150	1500	0	50	99.56	0.03
200/1400/50	200	1400	0	50	99.24	0.02
50/1400/100	50	1400	0	100	99.80	0.03
100/1400/100	100	1400	0	100	99.77	0.03
150/1400/100	150	1500	0	100	99.60	0.03
200/1400/100	200	1400	0	100	99.52	0.02
120/1320/5/30	120	1320	5	30	99.29	0.03

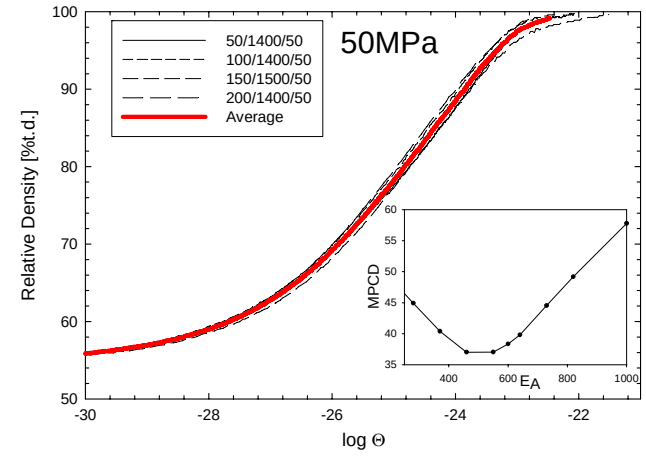
Note: s is standard deviation, n is number of measurement

The samples sintered with a pressure of 50 and 100MPa reached densities higher than 99% t.d.. The Figs. 2a-c show the MSCs constructed for constant pressures in the range from 20 to 100MPa. All constructed MSCs have a similar shape. Increased pressure shifts MSC to lower value of Θ, which means higher relative densities at the same temperature. It can be seen in Fig. 2, that all three MSCs were successfully constructed using the sintering activation energy of 600kJ/mol. There is a wide range of sintering activation energy (342-1064kJ/mol) reported in the literature [17-19]. This is probably caused by use of different initial powder, shaping technology, sintering conditions etc. Therefore the sintering activation energy established from this non-isothermal process is not a true material characteristic and we call it “apparent sintering activation energy”. Estimated activation energy in this work is in a good

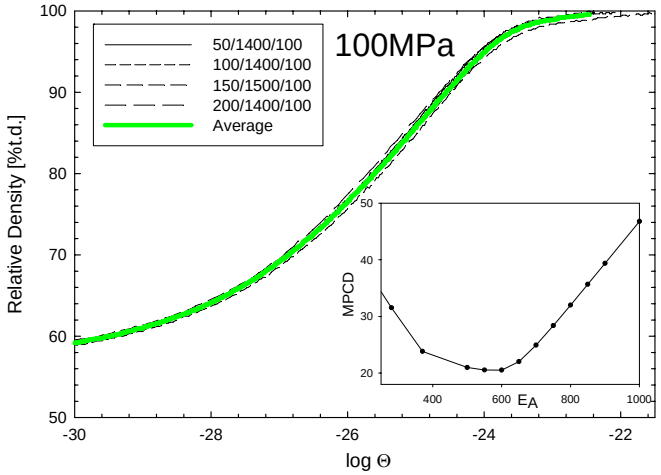
agreement with Aminzare (608kJ/mol) [20] who also used a MSC concept. The combination of the MSCs with constant pressures of 20, 50 and 100MPa leading to MSS construction is shown in Fig. 3. The calculated surface is smooth without any unexpected artefacts.



a)



b)



c)

Fig. 2 The MSC of alumina for SPS pressure of 20MPa and activation energy of 600kJ/mol (a), The MSC of alumina for SPS pressure of 50MPa and activation energy of 600kJ/mol (b), The MSC of alumina for SPS pressure of 100MPa and activation energy of 600kJ/mol (c)

One of the benefits of MSC and MSS is the possibility of densification prediction for any heating and pressure schedule. Fig. 4a and 4b compare the densification behaviour of experimentally measured sample 120/1320/5/30 (heating rate 120°C/min, final sintering temperature 1320°C for 5 minutes, applied pressure 30 MPa) with densification prediction via constructed MSS (Fig. 3). Although the chosen sintering schedule varied from previous experiments in heating rate, final temperature, dwell time and applied pressure, the difference between the predicted and measured values is in the range of about +/-0.2%t.d. This results fits densification process better than it was published by An et al. [21], who changed only the heating rate and a pressure, and they found deviation of 1%.

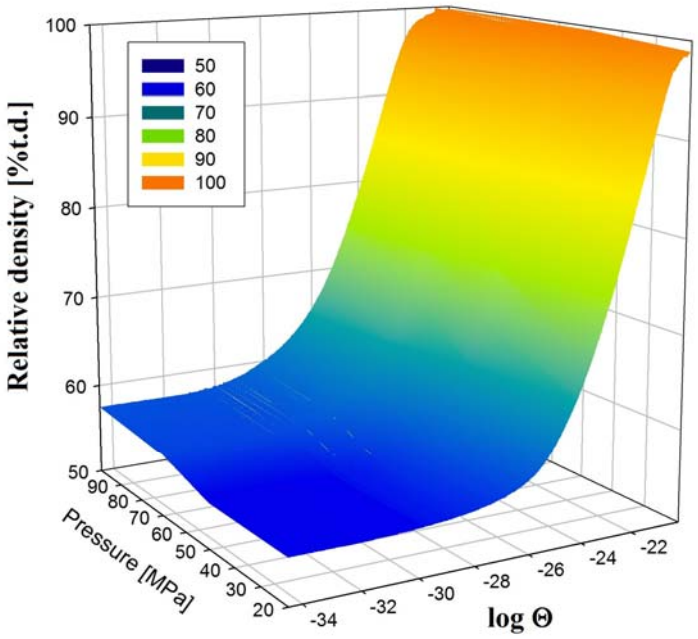


Fig. 3. The MSS of alumina ceramic sintered in SPS

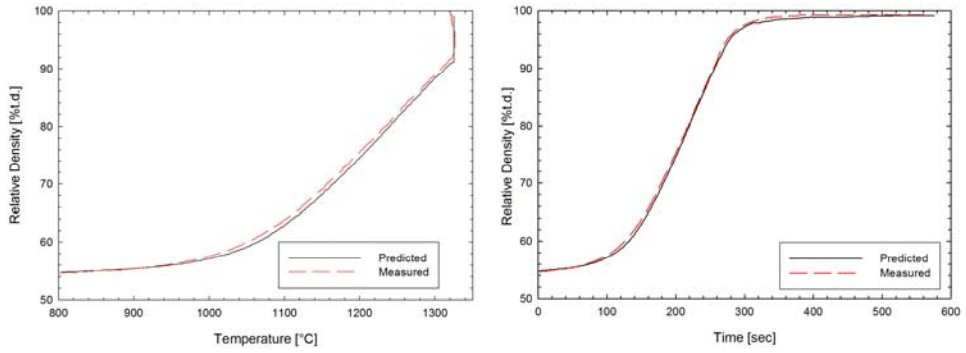


Fig. 4. The overlap between predicted and measured heating profiles for sample 120/1320/5/30 (heating rate 120°C/min, final sintering temperature 1320°C for 5 minutes, applied pressure 30 MPa)

4. Conclusion

It is shown in this study that the Spark Plasma Sintering can be described by Master Sintering Surface concept. The MSS construction was demonstrated using alumina powder

with a particle size of 300nm, for which the sintering activation energy of 600kJ/mol was established during SPS experiments. The calculations were done by newly developed software, which is also presented in this paper. The validity of created MSS was verified by successful prediction of alumina SPS kinetics.

Acknowledgement

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Садржај *Обзиром да је синтеровање комплексан процес, свака предикција понашања материјала током синтеровања је добро дошла не само у индустријске сврхе. Овај рад показује могућност предвиђања процеса згушњавања базиран на концепту Мастер синтеринг површине (МСП) код синтеровања у плазми. Приказан је и софтвер за израцунавање МСП. Овај концепт је коришћен за предикцију процеса згушњавања алумине током синтеровања у плазми.*

Кључне речи*: Плазма синтеровање, мастер синтеринг површина, кинетика синтеровања, алумина.*