

A Versatile Software for Construction of the Master Sintering Curve

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Abstract. Several models have been developed over the last years to study the microstructure development of ceramic and metal powders during sintering. Among the most utilized methodology one may find the Arrhenius and the so-called Master Sintering Curve (MSC). Both models involve manipulation of a large number of data, and repetitive and time-consuming calculations. In this work, was developed a versatile and friendly-user software for a PC-type computer encompassing both methodologies. The software is flexible allowing for kinetic data evaluation such as the activation energy for sintering and sintering maps. Details of the software along with its application to investigate the sintering process of 10 mol% gadolinia-doped ceria are described.

Introduction

Sintering is a key step in the development of ceramic and metallic components by powder metallurgy [1]. During sintering, continuous microstructure changes occur in the microstructure of powder compacts [1-3]. Sintering is useful to increase the mechanical strength of materials and are currently utilized to optimize their properties. To accomplish that, a rigid microstructure control is of primary concern. Several reports may be found in the literature related to the development of models allowing for predicting the microstructure evolution [4-7].

In this work, a friendly-user software for PC-type computer was developed for analysis of dilatometry data using both the Arrhenius method as modified by Wang and Raj [8], and the construction of the MSC [9]. The software allows for obtaining also the apparent activation energy for sintering as well as sintering maps. As an example of application, gadolinia-doped ceria data were analyzed using the software.

Master Sintering Curve. Su and Johnson [9] proposed a model to construct the Master Sintering Curve for density of materials, based on the combined sintering model in which the densification rate of a polycrystalline ceramic may be written as:

$$\frac{d\rho}{3\rho dt} = \frac{\gamma\Omega}{kT} \left(\frac{\delta_{cg} D_{cg} \Gamma_{Gcg}}{G^4} + \frac{D_v \Gamma_{Gv}}{G^3} \right) . \quad (1)$$

where ρ , γ and Ω are the density, the surface energy and the atomic volume, t , k and T are the time, Boltzmann constant and temperature, G and δ are the grain size and the grain boundary width, D and Γ are the diffusion coefficient and the lumped parameter, and the subscripts gb and v stand for grain boundary and volume. Manipulation of this equation for an isotropic diffusion, and assuming a single densifying mechanism (volume diffusion, for example), yields:

$$\int_0^t \frac{1}{T} \cdot \exp\left(\frac{-Q}{RT}\right) dt = \frac{k}{\gamma\Omega D_0} \cdot \int_{\rho_0}^{\rho} \frac{(G(\rho))^3}{3\rho\Gamma_G(\rho)} d\rho . \quad (2)$$

where the right-hand term depends only on the microstructure, whereas the left-hand term is a function of the activation energy for sintering (Q) and depends on the temperature/time profile. The left-hand term in equation (2) may be written as:

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

where $\Theta(t, T(t))$ is known as the work of sintering and characterizes the thermal history of the material. The relationship between $\Theta(t, T(t))$ and the density is the master sintering curve.

Construction of the MSC is done by integrating equation (3). Whenever the value of Q is unknown, the calculation involves several linear shrinkage curves with different heating rates. The corresponding density curves are calculated and an arbitrary value of Q is used to evaluate the MSC. This process is repeated a number of times for other values of Q until the mean residual square among the experimental and calculated data is reached. This minimum value will produce the convergence of the several linear shrinkage curves. Further details of the calculation may be found elsewhere [9].

Experimental

$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$, GDC (+99.5%, Fuel Cell Materials) with specific surface area $210 \text{ m}^2\cdot\text{g}^{-1}$ was used as received. Powder compacts were prepared by uniaxial followed by cold isostatic pressing (70 MPa) without organic binder.

Linear shrinkage measurements were carried out in a vertical dilatometer (Anter Unitherm™ model 1161) up to 1400°C with heating rates 3, 6, 10 and $12^\circ\text{C}\cdot\text{min}^{-1}$ and cooling rate $10^\circ\text{C}\cdot\text{min}^{-1}$. Correction for the thermal expansion of the dilatometer sample holder was obtained by measuring alumina Crystalox® as reference material. The thermal expansion of GDC was determined from the cooling curve of linear shrinkage measurements.

To validate the obtained results, green compacts were sintered in conventional oven (Lindberg BlueM) in the $600\text{-}1400^\circ\text{C}$ range for 0-15 h (0 stands for measurements with null holding time). The apparent density was determined by measuring sample mass and dimensions.

Software description. The software, *sintering fit*, was developed using MatLab platform. Initially the software reads the collected shrinkage data. The method for construction of the MSC is the non-linear least square, which allows for obtaining the limits of confidence of the adjusted parameters. The sequence of subroutines executed by the software is indicated in Fig. 1. Several corrections may be applied to experimental data such as: for thermal expansion of the dilatometer sample holder, and sample, mass loss, initial temperature, and fluctuations of the linear shrinkage at low temperatures (instrumental correction). Then, the density curves are calculated from corrected data. The work of sintering is then calculated for a fixed Q value. Fitting of the data proceeds via a polynomial [9] or a sigmoidal [10] function. Afterwards, the mean residual square is calculated for each fitting. As additional refinement, the best calculated mean residual square is introduced in a fitting algorithm using non-linear square method. This procedure minimizes the convergence to minimum locals.

The software allows also for determining the activation energy for sintering by the Arrhenius method [8] as well as construction of sintering maps.

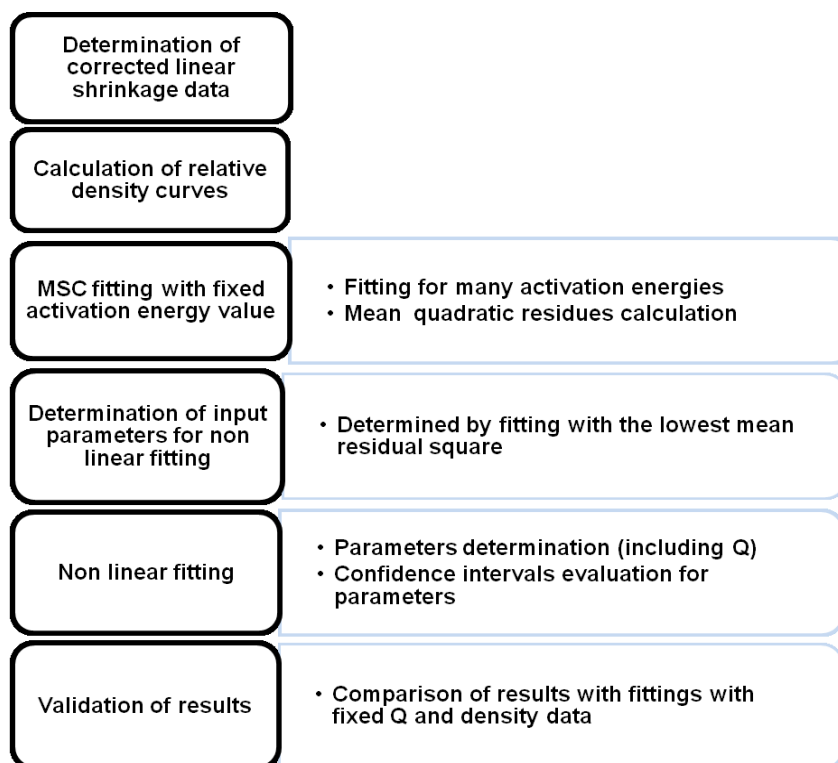


Fig. 1: Schematic flowchart of the algorithm for construction of the MSC.

Results and Discussion

Fig. 2 shows as example the screen output of the software with the calculated MSC for GDC. For this curve the polynomial function to fit experimental data was selected. The order of the polynomial function may be chosen by a significance test. The range of densities selected for the calculation may be arbitrarily chosen. The calculated activation energy for sintering is $590 \text{ kJ}\cdot\text{mol}^{-1}$. One may notice the excellent convergence of density data.

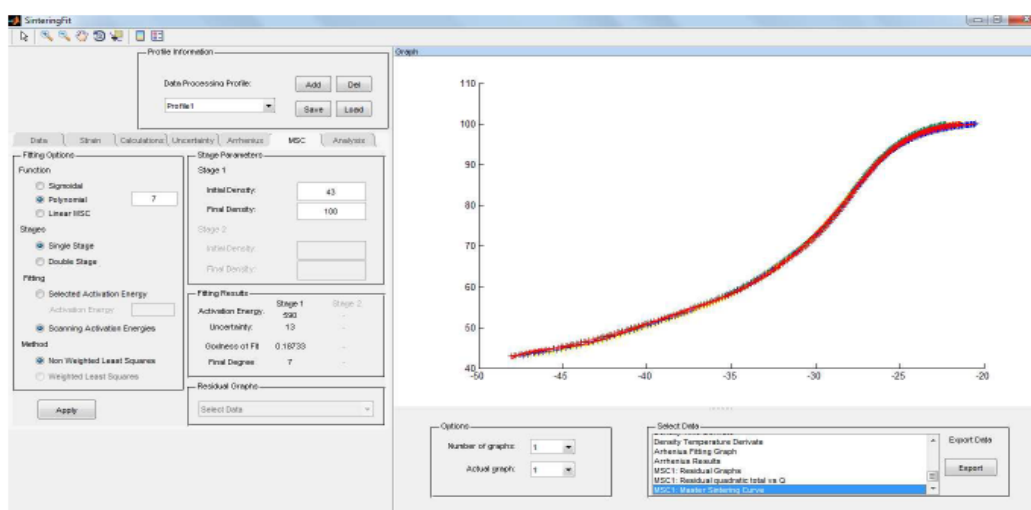


Fig. 2: Screen output of the *sintering fit* software showing the calculated MSC for GDC.

In this case the applied corrections were for the thermal expansion of the dilatometer sample holder and sample, and for mass loss. Correction for the mass loss was performed from data obtained from thermogravimetry.

Fig. 3 shows in a selected density range the calculated activation energy values from the Arrhenius method. In this method, the derivative curve of the linear shrinkage is used, which usually shows a significant noise. Then, an algorithm of moving average type was implemented in the software to smooth the derivative curve.

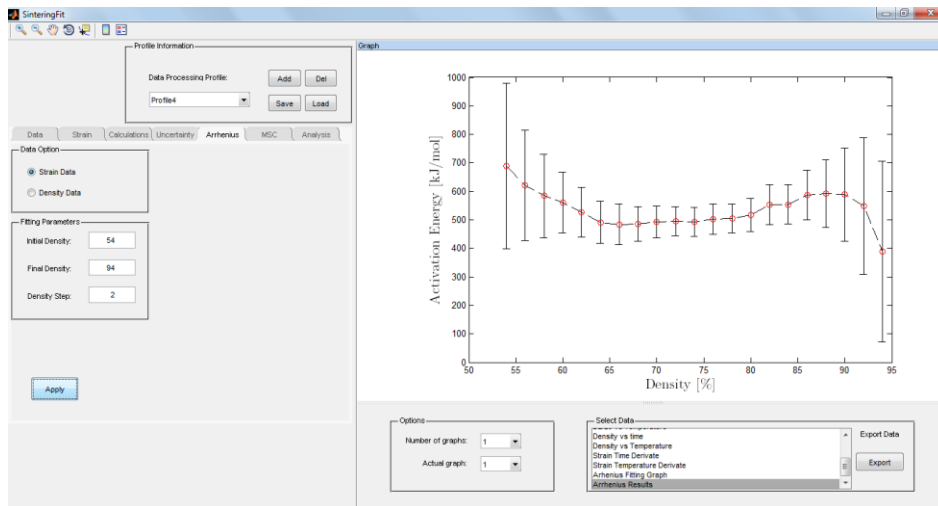


Fig. 3: Screen output of the *sintering fit* software showing the curve of activation energy values versus density for GDC.

One may observe, in the central region of the plot, a nearly constant activation energy value. In the low and high density ranges the activation energy deviates from the straight line with non-negligible scattering. This scattering is an indication of multiple sintering mechanisms acting on the powder compact in those ranges. This type of result may be useful to select a suitable range of densities for calculating the MSC. The value of activation energy obtained by the Arrhenius method is in agreement with that determined from the MSC within experimental errors ($\pm 40 \text{ kJ.mol}^{-1}$).

As example of sintering maps, Fig. 4 shows those curves obtained for a heating rate of $10^\circ\text{C.min}^{-1}$.

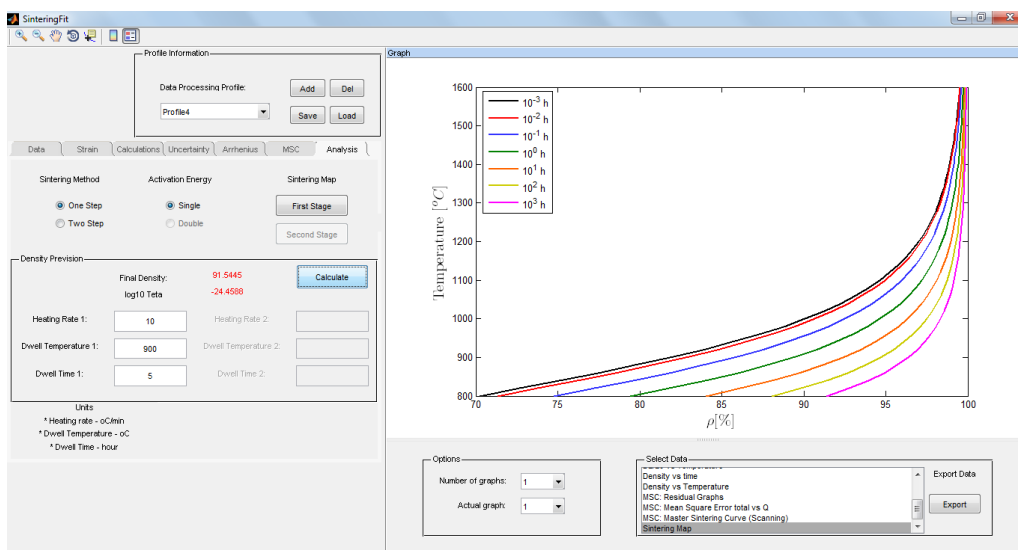


Fig. 4: Screen output of the *sintering fit* software showing sintering maps calculated for GDC using heating rate of $10^\circ\text{C.min}^{-1}$.

The heating rate and the dwell temperature are selected for calculations in the left-hand side rectangle. The software also allows varying the heating cycle in one or two stages.

Conclusions

A versatile and friendly-user software was developed to calculate the activation energy for sintering by the Master Sintering Curve and the Arrhenius methods. The software also allows for determining sintering maps. The software interface provides several corrections to be made to experimental data before calculating kinetic parameters of sintering. Data for a nanostructured GDC powder was analyzed by the software and an activation energy for sintering of 590 kJ.mol^{-1} was calculated.

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