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Sintering Densification Curve – a Practical Approach For Its Construction From Dilatometric Shrinkage Data

K. Maca^{1*)}, V. Pouchly¹, A. R. Boccaccini²

¹ Department of Ceramics and Polymers, Brno University of Technology, 616 69 Brno, Czech Republic

² Department of Materials, Imperial College London, London SW7 2BP, UK

Abstract:

This article summarizes the usage of high-temperature dilatometry in ceramic processing and powder technology with special attention on the description of the sintering process. A practical method for transformation of dilatometric shrinkage data into densification curves (the dependence of the sample density on sintering temperature or time) is described in detail. A new automatic procedure to recalculate sintering shrinkage data allowing the plot of the densification curve has been developed, which is presented here.

Keywords: *High-temperature dilatometry; Sintering shrinkage; Densification curve.*

1. Introduction

High-temperature dilatometry enables the heating of samples and the in-situ recording of sample dimension changes. Material elongation with increasing temperature is a natural and very important feature of all materials therefore the basic application of dilatometry is in the evaluation of the coefficient of thermal expansion (CTE) of materials [1-3]. Since phase transformations of materials at high temperatures are often accompanied by volume changes, the dilatometer can also serve as a convenient tool for the determination of the specific temperatures at which phase transformations occur [4, 5].

The sintering process is an essential step in ceramic processing and powder metallurgy. Sintering is associated with changes that occur in materials during firing, including variation of grain size and shape and changes in pore morphology and size [6]. These processes are accompanied by volume changes, i.e. shrinkage. Sintering in dilatometers has the advantage to enable continuous monitoring of specimen shrinkage, thus this method is often used in ceramic technology to determine sintering behavior of powder compacts [7]. Important theoretical models and basic knowledge can be derived from these evaluations [8, 9], e.g. the sintering activation energy can be calculated by this way [10, 11].

One particular sintering method, the so-called “rate controlled sintering” (RCS) [12], requires the help of high-temperature dilatometry. With the RCS method, the sintering of the specimen proceeds according to a predetermined time-dependence of density. The difference between actual and desired density is used to modify the heating power. The RCS method is an example of a process in which the shrinkage data gained from dilatometry have to be

*) Corresponding author: maca@fme.vutbr.cz

recalculated to determine the density changes.

From a practical point of view the dependence of density on sintering temperature and time (the densification curve) is a very important tool in sintering technology. The aim of this paper is to describe the transformation of dilatometric shrinkage data obtained during the sintering process into the curve giving the dependence of relative density on temperature and time. The automatic procedure of this calculation will be demonstrated for the temperature controlled sintering (heating with constant heating rate and dwell at the sintering temperature).

2. Calculation of densification curve from sintering shrinkage data

It is worthwhile reflecting on the changes that occur in a ceramic body during sintering. For simplicity, a material which does not undergo phase transformation is chosen and a sample sintering schedule with constant rate of heating and dwell at the sintering temperature is applied.

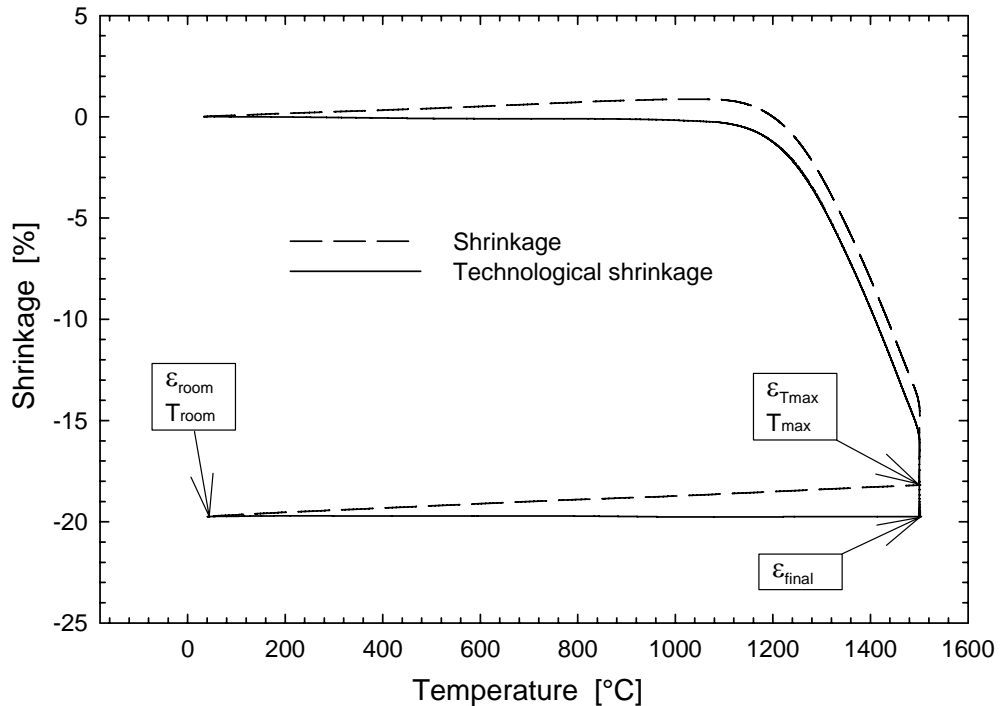


Fig. 1 The dependence of sintering shrinkage and technological shrinkage on temperature

A typical example of a sintering shrinkage curve is given in Fig. 1. At a low temperature only thermal dilatation of the green body is recorded. When a certain temperature is reached the sintering process begins and the material starts to shrink. As long as the temperature increases the thermal dilatation continues as well. During the dwell time at the sintering temperature the thermal dilatation is stopped, but shrinkage caused by the sintering process continues.

We can assume that during sample cooling sintering no longer takes place; therefore the cooling shrinkage is only dependent on thermal dilatation and we can calculate the coefficient of thermal expansion (CTE) from this part of the shrinkage curve:

$$CTE = \frac{\varepsilon_{room} - \varepsilon_{T_{max}}}{(T_{room} - T_{max})} \cdot 100, \quad (1)$$

where: ε_{room} is the shrinkage after cooling (%),
 $\varepsilon_{T_{max}}$ is the shrinkage at the end of the dwell (%),
 T_{room} is the temperature after cooling (°C),
 T_{max} is the temperature at the end of the dwell (°C).

Knowing the value of CTE, we can subtract the shrinkage caused by thermal dilatation and obtain the so-called technological (sintering) shrinkage:

$$\varepsilon_{techn.}(t, T) = \varepsilon(t, T) - CTE \cdot 100 \cdot (T - T_{room}), \quad (2)$$

where: $\varepsilon(t, T)$ is the actual shrinkage,
 t is the time,
 T is the actual temperature.

It can be seen from Fig. 1 that the technological shrinkage remains constant up to the onset of sintering and also during cooling.

To transform the temperature (or time) dependence of the technological shrinkage into the densification curve it is necessary to know the value of the sample density either before sintering (so called green density - ρ_{gd}) or after sintering (final density - ρ_f). This density can be measured accurately with the help of the Archimedes' principle (EN 623-2). If the green density of the sample is known, the shrinkage curve can be recalculated to the densification curve according to the Eq. (3):

$$\rho(t, T) = \rho_{gd} \cdot \frac{100^3}{(100 + \varepsilon_{techn.}(t, T))^3}. \quad (3)$$

Very often the sample after sintering does not contain open pores. In this case the final density can be measured easier and with more precision than the green density. Using the value of final density the recalculation of shrinkage data to density values is done using Eq.4, which is only slightly different to Eq. 3:

$$\rho(t, T) = \rho_f \cdot \frac{(100 + \varepsilon_{T_{max}})^3}{(100 + \varepsilon_{techn.}(t, T))^3}. \quad (4)$$

The values of ρ_{gd} and ρ_f can be expressed in the standard unit of mass per volume [kg/m^3 , g/cm^3] or in terms of relative density [% t.d.]. Relative density is the ratio of the actual density to the theoretical density (t.d.) of the material.

Eq. (3) and Eq. (4) describe the situation of isotropic shrinkage. There are however situations where the sintering shrinkage of the sample is different in different directions [13]. The reason for this behaviour can lie for example in nonhomogenous microstructure of the green body (it is often observed e.g after uniaxial dry pressing) or in the arrangement of nonspherical particles during special shaping methods (e.g. injection moulding or extrusion) [14]. The coefficient of shrinkage anisotropy can be defined by the ratio between axial and radial strains following Eq.(5):

$$K_1 = \frac{\varepsilon_a}{\varepsilon_l}, \quad K_2 = \frac{\varepsilon_b}{\varepsilon_l}, \quad (5)$$

where: $\varepsilon_a, \varepsilon_b$ are the final transversal (radial) sample shrinkages (%),
 ε_l is the final longitudinal (axial) sample shrinkage (%),

For anisotropic shrinkage behaviour, Eq. (4) is altered as shown below (Eq. 6):

$$\rho(t, T) = \rho_f \cdot \frac{(100 + \varepsilon_{T_{\max}}) \cdot (100 + \varepsilon_{T_{\max}} \cdot K_1) \cdot (100 + \varepsilon_{T_{\max}} \cdot K_2)}{(100 + \varepsilon_{\text{techn}}(t, T)) \cdot (100 + \varepsilon_{\text{techn}}(t, T) \cdot K_1) \cdot (100 + \varepsilon_{\text{techn}}(t, T) \cdot K_2)} \quad (6)$$

The densification curve calculated according to Eq. (6) using the shrinkage curve given in Fig. 1 and the values of $\rho_f = 99.14\% \text{ t.d.}$, $K_1 = K_2 = 1$ is shown in Fig. 2.

3. Automatic procedure of recalculation of sintering shrinkage data onto the densification curve

The aim of this part of the paper is to show an easy procedure of transformation of the dilatometric shrinkage curve into the densification curve. We would like to introduce the freeware program which automates all steps of calculation described above.

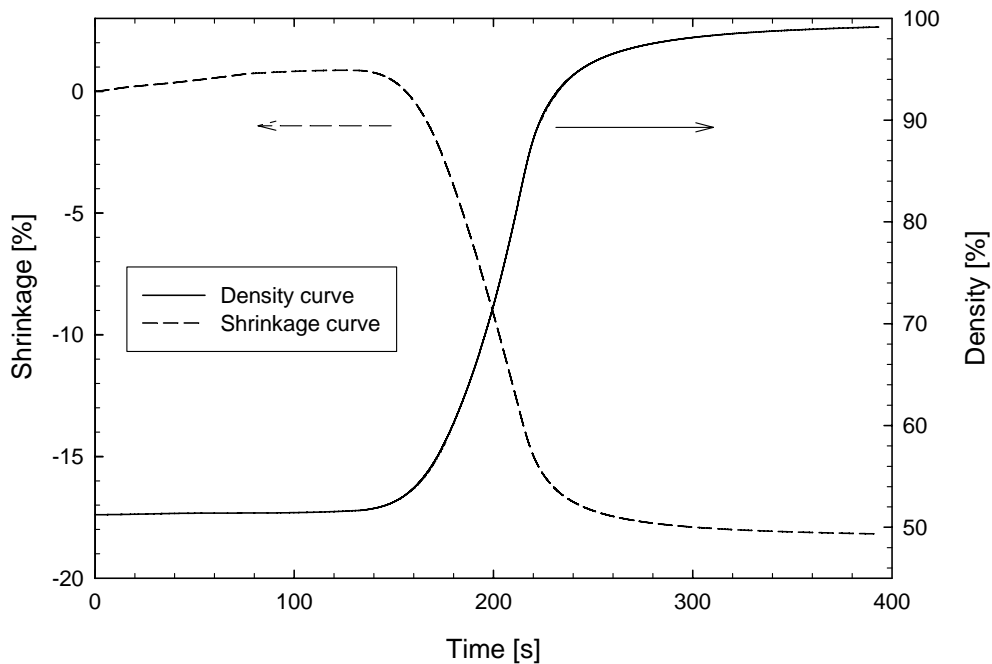


Fig. 2 The dependence of sintering shrinkage and relative density on time

The dilatometric shrinkage data $\varepsilon(t, T)$ can be imported either in ASC format or in XLS. After downloading the shrinkage data, the dependence of sintering shrinkage on temperature is displayed. The program is able to recognize the cooling curve and calculate the CTE (see Figs. 1 and 3a). The user has additionally the possibility to manually choose the points from which the CTE is calculated or set the fixed value of CTE.

Knowing the value of CTE and following Eq. (2) the program calculates the technological shrinkage and selects the likeliest point of final shrinkage for calculations given in Eq. (4). This point can also be manually selected by the user (Fig. 3b).

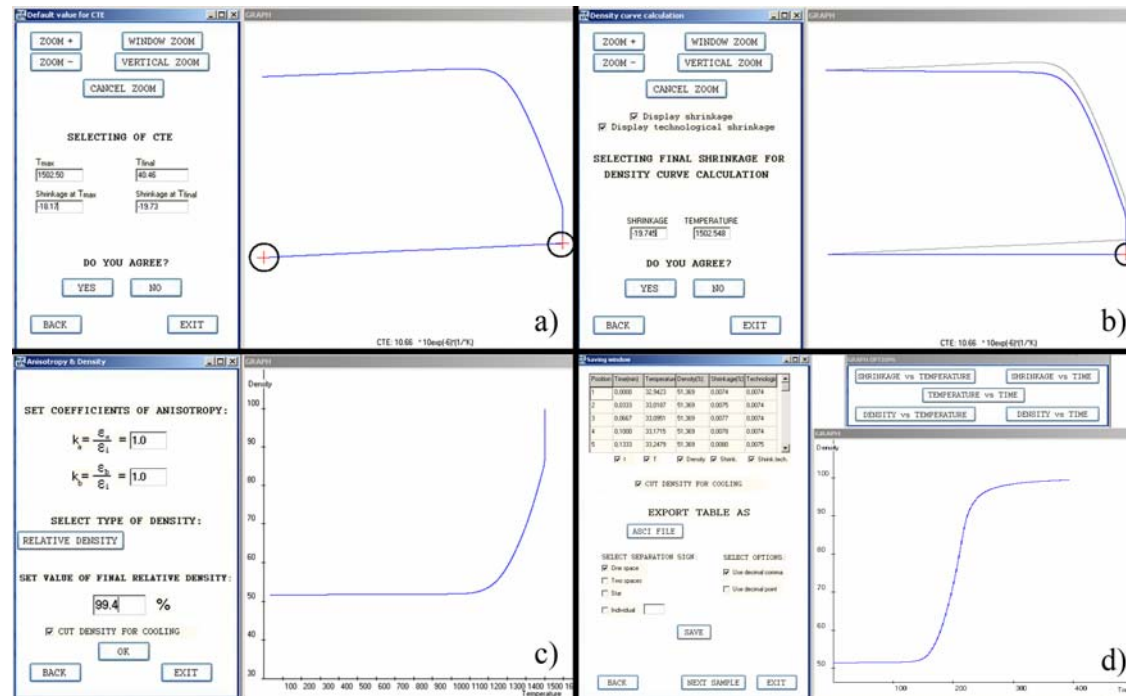


Fig. 3 Particular steps of the software “Density”

a) Calculation of CTE from cooling shrinkage; b) The dependence of sintering technological shrinkage on temperature and selecting of T_{max} ; c) Setting the values of shrinkage anisotropy coefficients and final density, and calculation of the densification curve; d) Export of results and view of various graphs

The final step consists of setting the values of coefficients of anisotropy (established from measuring the sample dimensions before and after sintering) and final (relative or absolute) density (measured by the Archimedes’ method). Subsequently, the program can apply Eq. (6) and finalize the calculation of the densification curve (Fig 3c).

The software generates also various graphs and the results can be exported in TXT, ASC or XLS formats (see Fig. 3d). This program is freeware and can be obtained by contacting the corresponding author.

4. Conclusion

An easy way to transform primary dilatometric sintering shrinkage data into densification curves was demonstrated and the automatic procedure of a computer program developed with this aim was described step by step. The new software presented here is readily available and it will be of use for researchers in the field of ceramic processing technology.

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Садржај: У овом чланку сумирано је коришћење високотемпературне дилатометрије у керамичкој обради и технологији прахова при чему је специјална пажња усмерена на опис процеса синтеровања. Детаљно је описана практична метода трансформације дилатометријских података о скупљању у криве згушњавања (зависност густине узорака од температуре или времена синтеровања. Презентована је нова аутоматска процедура за прерачунавање података о скупљању током синтеровања при чему је омогућено плотовање криве згушњавања.

Кључне речи: Високотемпературна дилатометрија, скупљање током синтеровања, крива згушњавања.
