



A dynamic bifurcation criterion for thermal runaway during the flash sintering of ceramics



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ABSTRACT

In this paper the densification of ceramics under flash sintering is modelled using an approach based on the heat equation coupled with a apparent activation energy kinetic equation for densification, leading to a system of nonlinear differential equations. Methods to analyse the system either by numerical solutions or via bifurcation theory are presented. Measurements needed to estimate sintering kinetic parameters are executed. The model shown explains the two main features of flash sintering: A characteristic electrical field threshold independent on the temperature, and an incubation time to flash sintering. The results are in agreement with experimental results obtained for Ytria Stabilized Zirconia and for nano-sized BaTiO₃. It confirms that the critical condition for the Flash phenomenon is rather the temperature dependent resistivity than the sintering kinetics.

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1. Introduction

Flash sintering is a recently developed method [1–8] in which ceramics can be sintered at low temperatures in a short time. It is a non-linear phenomenon, characterized by a sharp increase of the conductivity of the sample and simultaneous rapid densification under an electric field above a threshold temperature in a few of seconds. It has many interesting characteristics, including a critical electrical field strength for which the phenomenon is observed [1], and a certain incubation time [9] in which the electrical field should be maintained while the current increases nonlinearly.

The main mechanisms of flash sintering are still not well understood. Most of the first explanations are related to a sintering process activated via Joule heating [9] or local melting at the grain boundaries [10], but recent results and discussions have led to conclusions indicating that the temperatures obtained during flash sintering could not be high enough to explain thereby the densification behavior [6,7,11]. New mechanisms, such as the nucleation of defects embryos under the effect of polarization by the field, have been proposed to account for both, the higher conductivity and self-diffusion (sintering) observed [12].

Todd et al. [13] have used the thermal runaway concept to explain the nonlinear behaviour in the “flashing” of dense samples.

Their description of the phenomena is closely related to the heat equation described in this work, although not taking densification directly into account.

Zhang et al. [14] have also developed a thermal runaway criterion to explain flash sintering. The criterion is based on comparing the rates of joule heating with dissipation. It can predict the onset of the non-linear behaviour, but it does not make any distinction whether a steady state at a higher temperature without electric current control can be reached or not, such as observed for low electrical fields [6].

Most of our work was inspired by the treatment given to the thermistor problem in power surges [15] and by the stability analysis used to avoid explosions in chemical reactors [16,17], since it involves the critical conditions for thermal runaway and a critical non-linear behaviour after a threshold condition.

The present paper starts by stating the model formulation and assumptions. Then, it does a simplified analytical treatment of the theory presented using the concepts of stability and bifurcation. Measurements needed to estimate the sintering kinetics are made, and finally the numerical treatment of the complete equations is presented.

2. Model formulation and assumptions

In order to model the sintering process, all the sintering driving forces such as surface energy and species diffusion are lumped together in a phenomenological equation, where

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densification depends on the instant density, and gets slower at higher densifications. It does not take into account neck formation (stage I of sintering), since this does not lead to densification. This approach emulates most of the sintering in the second phase and the beginning of the third phase of sintering, where most of the densification occurs. It also depends on the temperature by a factor independent on the density (ρ):

$$\frac{d\rho}{dt} = \left(1 - \frac{\rho}{\rho_d}\right) G(T) \quad (1)$$

where $G(T)$ is an empirical kinetic smooth function (see below) which increases with increasing temperature, based on the increase of activated diffusivity as a function of temperature. ρ_d is the theoretical material density. Similar formulae were already used for the modelling of Electric Discharge Sintering [18].

The temperature evolution during flash sintering, not taking into account spatial distributions of temperature, is a balance between the heat generation by Joule heating and the heat losses, either by convection or radiation:

$$V\rho C \frac{dT}{dt} = VEj - L(T) \quad (2)$$

where E is the applied electrical field strength, j is the current density flowing through the sample, C is the thermal capacity, V is the volume of the sample and $L(T)$ is a smooth function only dependent on T , increasing with increasing temperature. They can be functions of the order of T in the case of convection or T^4 in the case of radiation cooling. They are the limiting bounds for slow and rapid heating, respectively.

It is worth noting that the sample's dimensions will change during the process due to densification. This also leads to a change in the instant current density and electrical field strength. Since an lumped temperature analysis is used, this shrinkage is modelled using the following expressions for volume, area and length dimensions, respectively:

$$V = V_0 \left(\frac{\rho_0}{\rho}\right) \quad (3)$$

$$A = A_0 \left(\frac{\rho_0}{\rho}\right)^{2/3} \quad (4)$$

$$l = l_0 \left(\frac{\rho_0}{\rho}\right)^{1/3} \quad (5)$$

where the subscript 0 relates to the dimensions and density of the green body before sintering. All the instances of geometrical constants, current density and electrical field in the remainder of this article are corrected using Eqs. (3)–(5).

In order to be able to determine a relationship between voltage and current, an Arrhenius-like relationship is used to model the resistance (R) dependence on the temperature. Data from Todd et al. [13] already shows this NTC (Negative Temperature Coefficient) behaviour in zirconia at high temperatures:

$$R = R_0 e^{\frac{\Delta E}{kT}} \frac{l}{A_c} \quad (6)$$

where l is the distance between electrodes, A_c is the sample cross-section, R_0 is the preexponential resistivity factor, ΔE is the resistivity activation energy and k is the Boltzmann constant.

Applying Ohm's Law and taking into account a linear relationship between density (ρ) and resistivity:

$$E \frac{\rho}{\rho_d} = Rj \quad (7)$$

It is assumed that the resistance on the sample is linearly dependent on the cross-sectional area available for conduction and consequently, in the situation where the green body has a low

densification, there will be a higher current density in a smaller inter-particle contact area.

Differentiation of (7) as a function of time leads to:

$$\frac{d\rho}{dt} \frac{E}{\rho_d} + \frac{dE}{dt} \frac{\rho}{\rho_d} = \frac{dR}{dt} j + \frac{dj}{dt} R \quad (8)$$

Which in turn, leads to the following relationships for the constant voltage regime (9) and the constant current regime (10)

$$\frac{d\rho}{dt} \frac{E}{\rho_d} = \frac{dR}{dt} j + \frac{dj}{dt} R \quad (9)$$

$$\frac{d\rho}{dt} \frac{E}{\rho_d} + \frac{dE}{dt} \frac{\rho}{\rho_d} = \frac{dR}{dt} j \quad (10)$$

Differentiating (6) leads to:

$$\frac{dR}{dt} = -R_0 e^{\frac{\Delta E}{kT}} \frac{l \Delta E}{A_c k T^2} \frac{dT}{dt} \quad (11)$$

Substituting (1), (11) and (6) in (9):

$$\frac{dj}{dt} = \left(1 - \frac{\rho}{\rho_d}\right) G(T) \frac{E}{R_0} e^{-\frac{\Delta E}{kT}} + \frac{\Delta E}{kT^2} j \left(\frac{Ej}{V\rho C} - \frac{L(T)}{V\rho C}\right) \quad (12)$$

From (6) and (7), it is possible to express the specimen temperature, due to furnace and Joule heating as a function of the current and electrical field:

$$T_j = \frac{\Delta E}{k \ln(E\rho A_c / jR_0 l \rho_d)} \quad (13)$$

Using the same procedure as in (12) for the constant current regime:

$$\frac{dE}{dt} = -R_0 e^{\frac{\Delta E}{kT}} \frac{\rho_d \Delta E}{\rho k T^2} \left(\frac{Ej}{V\rho C} - \frac{L(T)}{V\rho C}\right) j - \left(\frac{1}{\rho} - 1\right) G(T) \frac{E}{\rho_d} \quad (14)$$

Now the main challenge is to find suitable functions for $L(T)$ and $G(T)$. For the sintering temperature rate function, $G(T)$, this work is based on the Master Sintering Curve concept [19], where the sintering kinetics can be lumped, considering that only one mechanism is responsible for most of the densification, and in that case it is possible to use a simple Arrhenius type function with an apparent activation energy H , using the same form used for the resistance relationship (15). Dilatometry experiments at different heating rates (Section 6.1) were made in order to observe if the sintering behaviour of the zirconia powder used fits the relationship, and to determine the values of H and the preexponential factor G_0 :

$$G(T) = G_0 e^{-\frac{H}{kT}} \quad (15)$$

For the heat loss function, $L(T)$, two limiting cases can be studied: convection (16) and radiation (17)

$$L(T) = hA_t(T - T_0) \quad (16)$$

$$L(T) = \sigma \epsilon A_t(T^4 - T_0^4) \quad (17)$$

where, T_0 is the furnace temperature, h is the convection heat transfer coefficient, A_t is the surface area of the sample, σ is the Stefan-Boltzmann constant and ϵ is the emissivity of the material.

3. Stability of nonlinear systems

Stability analysis is a widely known method to understand the behaviour of a system of nonlinear differential equations [20]. It has many applications in the chemical industry [16,17], where the design of reactors of exothermic reactions is critical to avoid unstable operation points which can lead to explosions caused by the feedback loop of increasing heating and, therefore, rate of reaction.

The method is based on two main concepts: finding the stationary points of the system of differential equations and analysing the eigenvalues and eigenvectors related to those stationary points. In

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