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Sintering kinetic window for yttria-stabilized cubic zirconia

Vaclav Pouchly[a,1], Karel Maca[a,b,*]

[a] CEITEC, Brno University of Technology, Brno, Czech Republic
[b] Faculty of Mechanical Engineering, Brno University of Technology, Brno, Czech Republic

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ABSTRACT

The influence of two pressure less sintering methods (single-step sintering and two-step sintering) on the final microstructure of cubic ZrO_2 was studied. Two different theoretical models were applied for the evaluation of the activation energies of sintering and grain growth. Consequently, the comparison of established activation energies allowed us to discuss the existence of sintering kinetic window where the grain growth is suppressed, while sintering is still active. The results show the sensitivity of microstructural evolution of c-ZrO_2 to the sintering temperature. The improved microstructure (i.e., the highest density and lowest grain size) of c-ZrO_2 was obtained, when low sintering temperature together with long dwell were applied irrespective of the sintering regime used.

1. Introduction

The preparation of advanced ceramic materials with improved properties is one of the most desirable goal in ceramic processing. Such enhancement is usually achieved with reaching the maximum density of ceramics accompanied by the minimum grain size. These parameters have overwhelming influence on the strength [1], hardness [2], toughness [3] and optical transparency [4,5] of ceramics. However, the increase of relative density of ceramic materials is mostly obtained via high-temperature sintering process. Unfortunately, elevated temperature simultaneously leads also to the grain growth. Chen and Wang [6] published a novel approach called two step sintering (TSS) and by this method they successfully sintered Y_2O_3 to full density without grain growth. TSS consists of two subsequent steps. In the first sintering step the material is heated with a constant heating rate until all pores become subcritical and unstable against shrinkage (75–92% of relative density). In the second step the temperature is decreased by tens, or even hundreds of °C and the sample is further sintered for a period of about tens of hours to full density. The temperature of second step of sintering must be adjusted to the value when the densification still proceeds, but the grain growth is frozen. Sintering without grain growth can be obtained due to the difference between the activation energy of sintering (Q_s) and activation energy of grain growth (Q_{gg}). The temperature interval, where Q_s is lower than Q_{gg} (i.e., sintering is active, while grain growth is limited), is called sintering kinetic window [7,8].

The TSS concept has so far been tested in many ceramic systems with different success rate. The c-ZrO_2 system was chosen for this study due to the highest reduction of grain size in available literature by a factor of 7 [9] or 2 [10,11], while for example TSS of t-ZrO_2 or Al_2O_3 lead to a reduction of the final grain size by a factor of 1.1 [10] or 1.3 [7], respectively. The aim of this work is to evaluate Q_s and Q_{gg} for c-ZrO_2 and to discuss the existence of kinetic window for this material.

2. Theoretical background

2.1. Master sintering curve

For the evaluation of Q_s most often the master sintering curve (MSC) [12] and the model of Wang and Raj [13] are used. MSC was derived by Johnson and co-workers in 90's [12,14] from the physical sintering models and is expressed by the following formula:

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

where γ is the surface energy, Ω is the atomic volume, k is the Boltzmann constant, T is the thermodynamic temperature, G is the mean grain size, D is the coefficient of diffusion process (v for volume, b

* Corresponding author at: CEITEC, Brno University of Technology, Brno, Czech Republic. Fax: +420 541143202.
E-mail addresses: vaclav.pouchly@ceitec.vutbr.cz (V. Pouchly), maca@fme.vutbr.cz, karel.maca@ceitec.vutbr.cz (K. Maca).
[1] Fax: +420 541143202.

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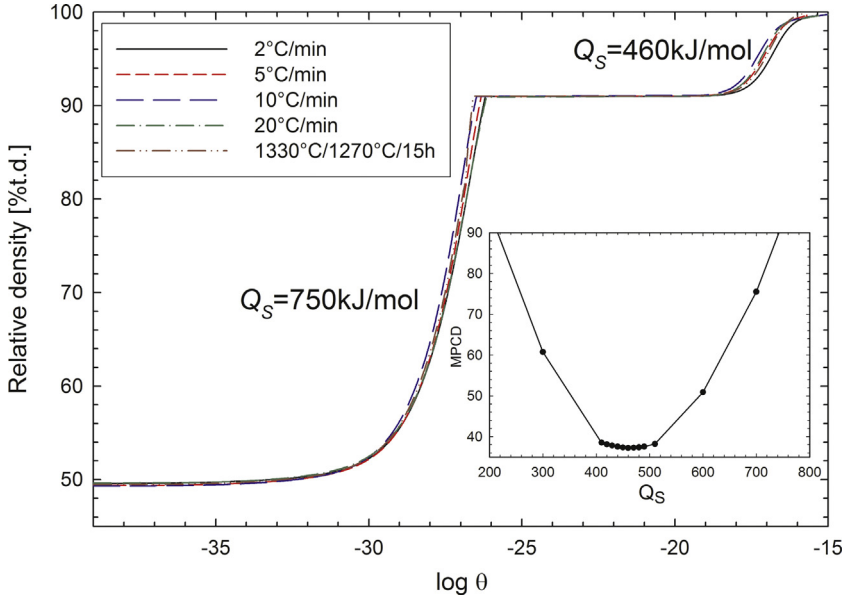

Fig. 1. Two-stage master sintering curve.

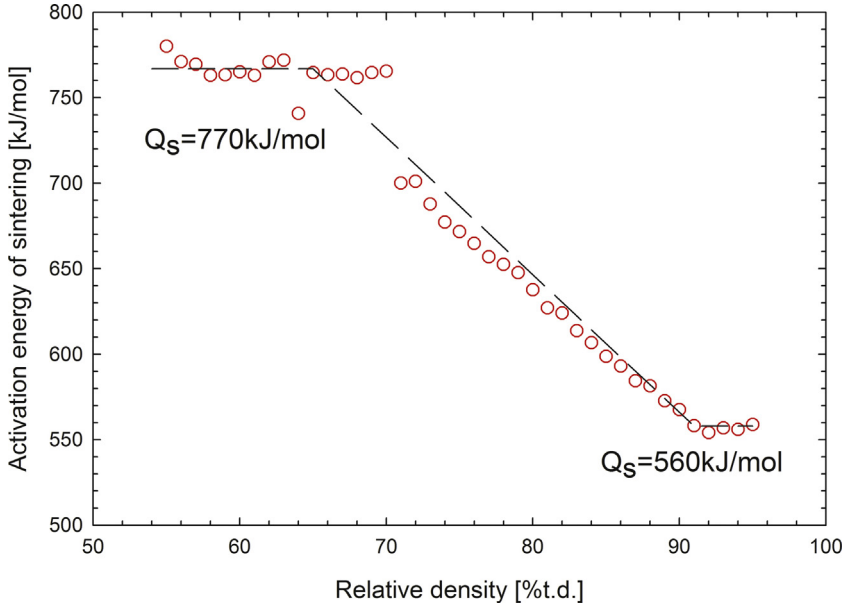

Fig. 2. Activation energy of sintering calculated from the model of Wang and Raj [13].

for boundary diffusion), Γ represents the scaling parameters that relate various geometric features, the driving force for sintering and the mean diffusion distance to the grain size, t is the time, δ is the width of grain boundary and L is the length of the sample.

In Eq. (1) two diffusion mechanisms are involved. If we assume that only one diffusion mechanism dominates the sintering process and the microstructure development (described by G and Γ) is a function of density only (regardless of used heating profile), then Eq. (1) can be rearranged to Eq. (2):

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

where ρ is the sample density, D_0 is the coefficient of the diffusion process (only one dominant diffusion process is assumed) and n has the value of 3 (for volume diffusion) or 4 (for grain boundary diffusion). The temperature/time dependence of density expressed in Eq. (2) is called master sintering curve (MSC). MSC is unique for a given powder which is shaped by the same technology.

Q_s can be calculated from Eq. (2) by measuring few densification curves with different heating schedules. If the concept of MSC is valid, there should exist only one Q_s for which all curves $\rho_i = f(\Theta_i)$ overlap and create one "master curve" for all heating schedules i.

2.2. The Wang & Raj model

The model of Wang & Raj is based on the model of Young and Cutler [15]. According to their model the densification rate can be expressed by Eq. (3):

$$\frac{\mathrm{d}\rho}{\mathrm{d}t}=A\frac{e^{-Q_s/RT}}{T}\frac{f(\rho)}{G^n}, \tag{3}$$