# Intensive particle rearrangement in the early stage of spark plasma sintering process

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## ARTICLE INFO

## ABSTRACT

The densification behaviors of 3 mol% yttria-stabilized tetragonal zirconia polycrystal (3Y-TZP) ceramics during spark plasma sintering (SPS) were analyzed both using the master sintering curve (MSC) approach and by evaluating the temperature dependent evolution of density and densification rate. It was found that densification curves could hardly be fitted using one apparent activation energy value by MSC conception, by which it indicated that more than one densification mechanisms were involved in SPS. Moreover, dependent neither on applied pressure (20–100 MPa) nor heating rates higher than 50 °C/min, the maximum densification rate had always been observed at rather similar ~78% of theoretical density (TD) accompanied with negligible grain growth. An intensive particle rearrangement mechanism was proposed to dominate the rapid densification to 78% TD in early stage of SPS process, by which it yielded the considerable faster densification rate than those achievable by diffusion-related processes.

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## 1. Introduction

As one of the most successful techniques for nanoceramic preparation, spark plasma sintering (SPS) has attracted increasing attentions not only for material processing but also in exploring the mechanisms underlying fast sintering [1–3]. Although possible contributions from plasma [4], electric field [5], heating rate [6], and pressure [7] have been widely investigated, a universal explanation for the rapid densification achievable by SPS is still unavailable. A general observation is the unusual high densification rate achieved in the early and intermediate stage of SPS, during which the density rapidly increases from ~50% to ~90% of the theoretical density (TD) accompanied with rather limited grain growth. The maximum densification rate achievable during this stage of sintering is often in the order of $10^{-3}$/s for solid-state sintering [8], and up to $10^{-2}$/s in liquid-phase sintering conditions [9]. Such high densification rates have hardly been achieved in conventional pressure-assisted processes. Moreover, the densification rate dramatically decreases by one order of magnitude during the final stage of sintering [8]. Neither the underlying densification mechanism(s) nor relationship of individual sintering stages has been well distinguished, yet. Using four classic pressure-assisted models, Xu et al. [10] reported that the effective activation energies for early densification in SPS were considerably lower than that expected for any diffusion-related process. In those regards, possible mechanism(s) besides the classic atomic diffusion-related processes was suspected to be involved in SPS process. The radical change of densification rate might reflect the switching of different densification mechanisms that dominate different sintering stages.

Master sintering curve (MSC) was developed to predict the sintering behaviors of powder compacts [11,12]. Focusing on the similarities among the three sintering stages, this model describes the whole densification process by one mechanism, thus also one equation:

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

where $\gamma$ is the surface energy, $\Omega$ is the atomic volume, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $G$ is the mean grain size, $t$ is the time, $L$ is the sample length, $D_v$ is the coefficient

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of volume diffusion, $D_b$ is the coefficient of grain boundary diffusion, $\delta$ is the thickness of grain boundary, and $\Gamma_v$ and $\Gamma_b$ represent geometric factors as the driving force in sintering. With the presumptions that microstructure evolution (represented by $\Gamma$ and $G$) is the function only of density independently on thermal history and that the whole densification process is dominated by only one mechanism based on atomic diffusion, the previous equation can be rearranged to follow the formula:

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

where $E_A$ is the apparent activation energy and $\rho$ is a density derived from linear sintering shrinkage. It is noted that the MSC cannot be fitted with single $E_A$ value when more than one densification mechanisms are involved in a sintering process [13]. This fact is used in the present work to reveal different sintering mechanisms eventually involved in the SPS process using 3 mol% yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) nanoceramics as examples.

## 2. Experimental procedure

Commercial 3 mol% yttria doped zirconia powder (TZ-3Y-E, Tosoh Co. Ltd., Tokyo, Japan) was used as the precursor material. As-received powder was in the form of spherical granules formed by thermal spray drying with a diameter ranging 60–120 μm. The initial crystallite size of the powder was 27 nm calculated from X-ray diffraction (XRD) peak broadening. The SPS process was carried out in a spark plasma sintering apparatus (Dr. Sinter 2050) in vacuum. Each batch of 1.0 g powder, without any further treatment, was poured into the cylindrical graphite die with an inner and outer diameter of 12 mm and 30 mm, respectively. A uniaxial pressure was automatically loaded to the targeted value of 20–100 MPa during the initial 3 min and kept constant to the end of each sintering cycle. The temperature was measured and regulated by a pyrometer focusing on the surface of graphite die. The samples were firstly automatically heated to 600 °C for 3 min and then to 900 °C at a heating rate of 100 °C/min, thereafter a range of heating rates from 10 to 200 °C/min was applied to obtain different prototypes.

The relative density was measured by Archimedes method taking 6.08 g/cm³ as the theoretical density of 3Y-TZP ceramics. The values of apparent activation energy $E_A$ of densification were established with the help of MSC concept. The best overlap of individual curves $\rho = f(\Theta_i)$, where $\Theta_i$ represents individual heating schedule, was found by minimizing the Mean Perpendicular Curve Distance (MPCD) [14]. The densification rate $r$ was calculated as $r = d\rho/dt$ (s$^{-1}$), where $\rho$ and $t$ are relative density and time, respectively. Field-emission scanning electron microscope (FE-SEM, JSM7400, JEOL Co. Ltd., Tokyo, Japan) was used to characterize the microstructures during sintering. To avoid possible mechanical artifacts, the grinded samples were further polished by an argon ion beam (SM-09010 Cross-section Polisher, JEOL Co. Ltd., Tokyo, Japan), which was operated at 5 kV/90 μA for 10 h. The ion-milled surfaces were further annealed for 30 min at 950 °C in air to expose grain boundaries before SEM observations. The average grain size of the samples prepared under different conditions was statistically measured based on recorded images by linear intercept methods without correlation factor used.
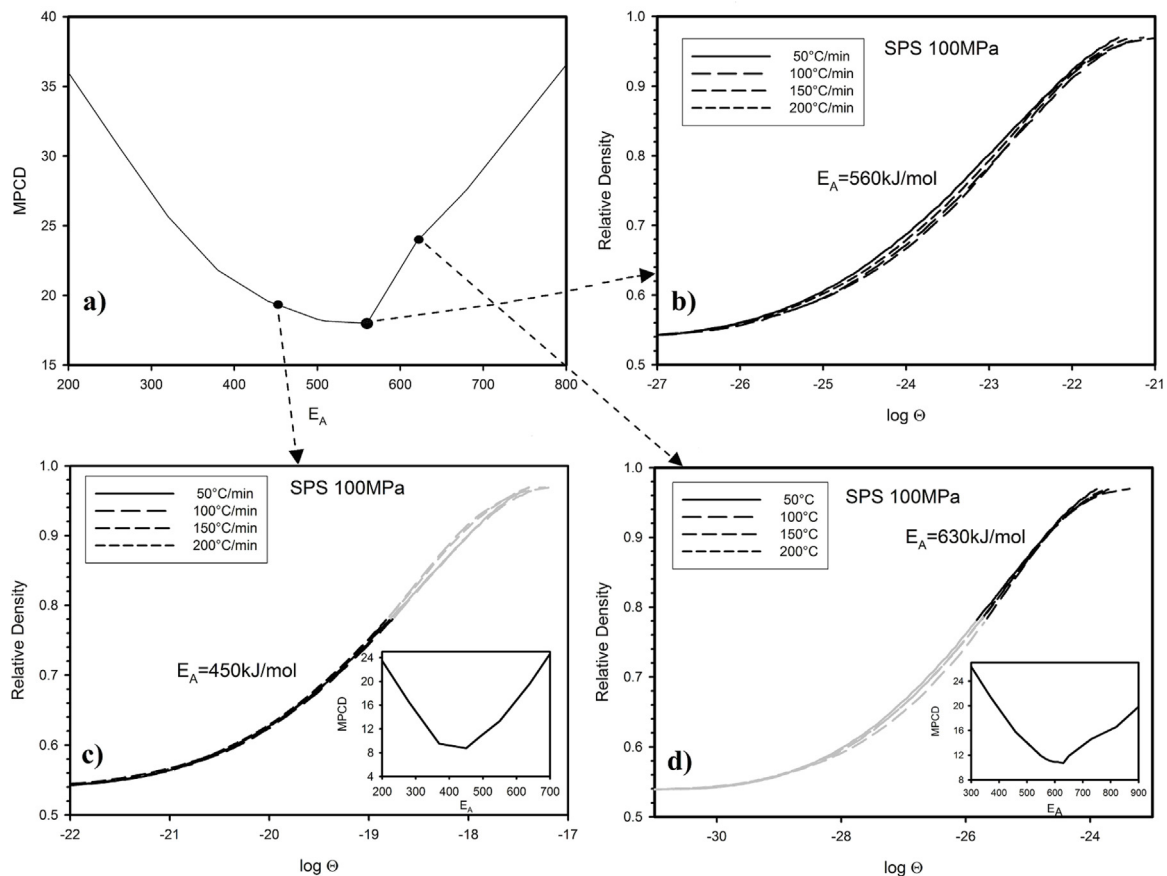


**Fig. 1.** The master sintering curve (MSC) evaluation of the sintering curves recorded during SPS process under 100 MPa pressure and with heating rate of 50, 100, 150, and 200 °C/min.