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Probing the densification mechanisms during flash sintering of ZnO

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ABSTRACT

Using ZnO as a model system, the densification mechanisms of flash sintering are investigated. Controlled experiments via limiting the maximum current or the effective ramp rate suggest that both the maximum specimen temperature and the high heating rate (on the order of 200 °C/s) are essential for the rapid densification during the flash sintering. Moreover, benchmarking rapid thermal annealing (RTA) experiments, which were conducted to mimic the heating profiles in the flash sintering, achieved similar densification and grain growth rates with comparable heating profiles, attesting that the ultrafast densification is mainly enabled/determined by the $T(t)$ profile. The combination of these experiments suggest that, at least for ZnO, the rapid heating profile is a key factor for the observed rapid densification in flash sintering, while various electric field/current effects could also exist. A clear and consistent correlation between the grain sizes and relative densities is also evident for specimens made by both flash sintering and RTA with different conditions, suggesting the same conventional grain growth mechanism in both cases under the current experimental conditions.

1. Introduction

Flash sintering, which was invented by Raj and his colleagues in 2010 [1], has attracted great scientific and technological interests in the last several years. It has major technological advantages with low furnace temperatures and high densification rates (short sintering duration), thereby being an energy-saving sintering technology. Moreover, flash sintering could be applied to numerous materials with a broad range of applications, including fuel-cell materials [2–4], electronic ceramics [5–8], structure ceramics [9,10], and solid electrolytes for lithium or sodium batteries [11]. Most recently, Saunders et al. introduced a ultrafast-contactless flash sintering method using plasma electrodes [12].

In a typical flash sintering experiment, an electrical field is applied to a specimen that is heated at constant ramp rate in a furnace. A flash occurs at a particular temperature with abrupt and simultaneous increases the specimen conductivity and temperature. Subsequently, the power control switches to a constant-current mode with a pre-set maximum current that sets the steady-state specimen temperature and densification completes in a few seconds.

Since flash sintering has many technological advantages and potential applications, a systematic and in-depth understanding of underlying mechanisms is crucial for its further development as well as the selection of materials and processing recipes. Specifically, three key scientific questions should be answered. First, how does a flash start? Second, what are the mechanisms for rapid densifications? Third, what are the electric field/current effects on sintering and microstructural development?

Several recent studies from different groups [5,6,13–16] suggested that the flash starts as a coupled electric and thermal runaway, at least for a range of materials systems that had been investigated. We should point out that these models do not rule out the possibilities that in certain materials, a thermal runaway may occur as a consequence of an avalanche of non-equilibrium defects or first-order bulk or interfacial transition that result in an abrupt increase in the specimen conductivity; yet, the thermal runaways can also (often) occur "naturally," *i.e.*, being triggered by the exponentially increasing specimen conductivity with increasing temperature, which have been observed in several prior studies [5,6,13–16].

This study focuses on the second question to probe the rapid densification mechanisms in flash sintering of ZnO, following several earlier studies. A prior analysis concluded that the estimated specimen temperature from Joule heating was not high enough to be responsible for the rapid densification observed in Y_2O_3-stabilized ZrO_2 (YSZ) [17], thereby suggesting other effects such as a possible avalanche of non-equilibrium Frenkel pairs.

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Majidi and van Benthem reported the enhanced shrinkage of particle agglomerates under a "non-contacting electric field" in an *in-situ* STEM experiment, implying an electric effect on promoting sintering [18]. In a series of elegant studies, Chen et al. demonstrated that surface diffusion of Zr cations leads to ionomigration of pores and low-temperature electro-sintering of 8YSZ [19–21]. For semiconductors such as ZnO, an applied current will lead to a (small) accompanying heat flux due to the Peltier effect, which should not affect the steady-state temperature distribution (and presumably sintering) significantly.

In this study, we investigated the flash sintering mechanisms of ZnO – a wide bandgap semiconductor with electronic conduction with significantly-enhanced conductivity at particle surfaces due to the excess surface electrons (~10^{12} electrons per cm^2 at the ZnO free surfaces) [22], which differ from the ionically-conducting YSZ systems that have been investigated more extensively in prior studies. We confirmed that the flash starts as coupled electric and thermal runaway in ZnO (as we had already demonstrated previously [6]), thereby leading to a ultrahigh heat rate (~200 °C/s) before reaching a steady-state stage where the specimen temperature is largely set by the maximum current limit. Specifically, controlled flash sintering experiments, where we limited either the maximum current or the effective heating rate electronically to probe the sintering mechanisms, suggest that both the steady-state specimen temperature and the ultrafast heating rate play critical roles for the rapid densifications in flash sintering of ZnO. Further critical comparison with rapid thermal annealing (RTA, with IR heating) experiments conducted using similar heating profiles (without electric flied/current) showed that the densification rates and grain growth are comparable. Moreover, the grain sizes *vs.* relative densities follow the same correlation for a large number of specimens made by both flash sintering and RTA with different conditions, suggesting the same conventional grain coarsening mechanism in both cases, where grain growth takes off after achieving ~90% relative density. These experiments collectively suggested that a rapid heating profile is a key factor for the observed rapid densification in the flash sintering of (at least) ZnO (under the current electric field/current conditions), while we recognize the possible existence of various electric field/current effects that can vary significantly for different materials systems.

2. Experimental procedure

2.1. Preparation of green pellets

The procedure of making green specimens has been described in prior reports [5–7] and is briefly summarized here. High-purity ZnO powders (>99.99%, purchased from Sigma Aldrich) with 0.5 wt % of a binder were grounded and uniaxially pressed at ~300 MPa to make pellets of D (diameter) = 6.4 mm and H (height/thickness) ≈ 3 mm for flash sintering. After burning out the binder, platinum was sputtered on both sides of the green specimens and surrounding areas were slightly grounded by SiC papers. The green specimens for rapid thermal annealing experiments have the same diameter (D = 6.4 mm) but are thinner (H ≈ 1 mm) to ensure uniform heating. The grain sizes of green specimens were measured to be ~120 nm from cross-sectional images using scanning electron microscopy (SEM).

2.2. Conventional flash sintering

The specimens were placed in a dilatometer (DIL 402 PC, Netzsch, Boston, MA, USA) and attached to two flatted Pt foils on both sides to apply electric fields. A programmable DC power supply, purchased from Ametek Inc. (model Sorensen DLM 300–10, San Diego, CA), was used to apply electric fields/currents in the flash sintering experiments. A minor pressure of ~9.55 kPa was applied (to ensure a good contact with the specimen) to measure the shrinkage of the specimen with the spatial resolution of ~8 nm. Conventional flash sintering was conducted on one set of specimens, where an (initial) electric field of $E_{initial}$ = 300 V/cm was applied and placed in the dilatometer with a constant heating rate of 5 °C/min (for the furnace temperature), until a flash event occurred and the current reached a preset maximum value (I_{max} = 0.5, 0.75, or 1 A, corresponding to the estimated current density of J_{max} ≈ 20, 30, or 39 mA/mm^2); after the I_{max} was reached, the power source switched from the voltage-control to the current-control mode (and the electric field dropped). After the current reached the I_{max}, the specimen was kept at this constant current mode for a preset duration (typically ≤ 30 s); then, both the electric power source and furnace were shut down and the specimen was cooled (rapidly) in the furnace.

2.3. Controlled flash sintering

In a flash sintering experiment with a controlled effective ramping/heating rate, an electroded specimen was placed in a dilatometer in the same configuration as a conventional flash sintering. An initially constant electric field of 300 V/cm was also applied. In this experiment, the maximum current limit was initially set to be 0.05 A; after the flash, the current limit was held for 100 s and then increased stepwise by 0.1 A per step; this process was repeated for seven steps until reaching the final I_{max} = 0.75 A. Then, the electric power source and furnace were shut down and the specimen was cooled in the furnace.

2.4. Conventional sintering

One specimen (without sputtered Pt electrodes) was also sintered in the dilatometer from room temperature to 1200 °C with a constant heating rate of 5 °C/min as a benchmark.

2.5. Rapid thermal annealing (RTA) experiments

Specimens (without sputtered Pt electrodes) were placed on a Pt foil in the rapid thermal annealing (RTA) equipment (AG Associates Heat Pulse 610) with IR heating. The heating ramp rate was set to be 200 °C per second; the specimens were then held (sintered) isothermally at 1000 °C and 1100 °C, respectively, for 0, 5, 10, 15, 20, 25, and 30 s, respectively.

2.6. Characterization

Bulk densities were measured by the standard Archimedes method if the density is greater than 90% without open porosity (and we have verified that all the densities measured by the Archimedes method agreed with those calculated by the weight and volume within the typical experimental errors). Otherwise, the densities were calculated by the weight and volume. The microstructure was characterized by a field emission environmental SEM (Philips XL30). Grain sizes were measured at the fractured surfaces using a standard intercept method from the SEM micrographs. Each measurement used images taken from 2 to 3 different locations in the center part of each specimen; the grain sizes and microstructure are largely uniform at different locations (other than the <100 μm thick surface layers adjacent to the electrodes). Electric conductivities of a flash-sintered specimen were measured by a digital multimeter (Tektronix DMM 4050, Beaverton, OR, USA) with a heating rate of 10 °C/min up to 1200 °C in the same configuration in the dilatometer to provide a second method to estimate