Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 94 (2015) 87–100
Acta MATERIALIA
www.elsevier.com/locate/actamat

Thermal runaway, flash sintering and asymmetrical microstructural development of ZnO and ZnO–Bi_2O_3 under direct currents

Yuanyao Zhang,[a,b] Jae-Il Jung[b,c] and Jian Luo[a,b,*]

[a] *Department of NanoEngineering, Program of Materials Science and Engineering, University of California, San Diego, La Jolla, CA 92093, USA*
[b] *Department of Materials Science and Engineering, Clemson University, Clemson, SC 29634, USA*
[c] *Interdisciplinary School of Green Energy, Ulsan National Institute of Science & Technology (UNIST), Ulsan 689-798, South Korea*

Received 29 September 2014; revised 9 April 2015; accepted 12 April 2015

Abstract—DC flash sintering of both pure and 0.5 mol.% Bi_2O_3-doped ZnO at a relatively high activating field of 300 V/cm has been investigated. It is demonstrated that even high-purity ZnO single crystals can "flash" at ~870 °C. In comparison, flash sintering occurs at a substantially lower onset temperature of ~550 °C in ZnO powder specimens, indicating the important roles of surfaces and/or grain boundaries. A model has been developed to forecast the thermal runaway conditions and the predictions are in excellent agreements with the observed onset flash temperatures, attesting that the flash starts as a thermal runaway in at least these ZnO based systems. Interestingly, enhanced grain growth is observed at the anode side of the pure ZnO specimens with an abrupt change in the grain sizes, indicating the occurrence of electric-potential-induced abnormal grain growth. With a large current density, the growth of aligned hexagonal single-crystalline rods toward the anode direction is evident in the ZnO powder specimen. Moreover, Bi_2O_3 doping defers the onset of flash sintering, which can be explained from the formation of space charges at grain boundaries, and it homogenizes the microstructure due to a liquid-phase sintering effect. The key scientific contributions of this study include the development of a model to predict the thermal runaway conditions that are coincident with the observed onset flash sintering temperatures, the clarification of how flash starts in ZnO based specimens, and the observation and explanation of diversifying phenomena of sintering and microstructural development under applied electric currents.

Keywords: Abnormal grain growth; Flash sintering; Microstructure; Sintering; Thermal runaway

1. Introduction

Recently, field-assisted sintering technology (FAST), also known as spark plasmas sintering (SPS) and pulsed electric current sintering (PECS), has attracted great interest because it can achieve high sintered density at a lower temperature in a shorter time with an improved microstructure [1–6]. In 2010, Raj and colleagues invented "flash sintering" [6,7], in which they used an electric field (20–100 V/cm) to initiate rapid densification of 3YSZ (3 mol.% Y_2O_3-stabilized ZrO_2) in just a few seconds at hundreds of degrees below the normal sintering temperatures. Subsequently, flash sintering was demonstrated for 8YSZ (an ionic conductor) [8], Co_2MnO_4 (an electronic conductor) [9,10], $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF, a mixed ionic electronic conductor) [11], $SrTiO_3$ (a dielectric oxide) [12], MgO-doped Al_2O_3 (but not pure Al_2O_3) [13], MnO_2-doped SnO_2 (but not pure SnO_2) [14], SiC-Al_2O_3–Y_2O_3 (but not pure SiC or SiC–Al–B_4C–C) [15], TiO_2 [16], $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) [17], and Y_2O_3 [18], An applied stress can further reduce the sintering temperature in flash-sinterforging [19]. Researchers also reported similar flash sintering (grain welding) effects induced by applied AC electric loadings using YSZ and $BaCe_{0.8}Gd_{0.2}O_{3-\delta}$ specimens, where they argued that the current flow though the specimens (instead of the electric field) is the key parameter [20–22].

Flash sintering differs from FAST because the applied electric field is typically higher, the sintering time is shorter, and the furnace temperature is lower. Thus, flash sintering can in principle be more cost-effective and energy-efficient. A mechanism for flash sintering must explain the simultaneous and discontinuous increases in mass transport kinetics and electrical conductivity. Originally, Raj et al. proposed three possible mechanisms [7]: flash sintering may be related to (1) Joule heating at grain boundaries that enhances grain boundary diffusion and electrical conductivity; (2) an avalanche nucleation of Frenkel pairs driven by the applied field; and/or (3) a non-linear interaction between intrinsic fields (space charges at grain boundaries)

---

[*] Corresponding author at: Department of NanoEngineering, Program of Materials Science and Engineering, University of California, San Diego, La Jolla, CA 92093, USA; e-mail: jluo@alum.mit.edu

http://dx.doi.org/10.1016/j.actamat.2015.04.018
1359-6462/

and the applied field that produces “a catastrophic change in self-diffusion at grain boundaries” [7]. More recent studies attributed the rapid sintering to a combination of Joule heating and defect generation (including possibly unconventional avalanches of Frenkel defects) [6,13,18,23] or enhanced ionic and electronic transport long selectively-heated (and even selectively-melted) grain boundaries and dislocations [24]; it was argued that that Joule heating alone is not sufficient for accounting for the observed fast densification [6,13,18,23]. Chen and co-workers proposed electro-sintering of 8YSZ is due to ionomigration of pores resulted from surface diffusion of cations [25–27]. In this study, we proposed a model to predict the thermal runaway temperature that is coincidental with the observed onset flash temperature, thereby attesting that the flash (at least) starts as thermal runaway in ZnO.

Furthermore, recent “two-electrode experiments” revealed interesting and intriguing observations of the field effects on grain growth [6]. Conrad and colleagues showed that a relatively weak applied DC or AC field could inhibit grain growth of 3YSZ significantly [28–32]. Consequently, sintering is enhanced because a smaller grain size provides a greater driving force. In a separate controlled experiment, Raj and colleagues also suggested that an applied modest DC field of ~4 V/cm can inhibit the grain growth in 3YSZ [33]. Two mechanisms have been proposed: Conrad explained this field phenomenon by the reduction in the grain boundary energy through interactions of the applied fields with the space charges near grain boundaries [30,31]. An alternative explanation was that Joule heating at grain boundaries raised the local temperature and reduces grain boundary energy by an entropic effect; this not only reduced the driving force, but also created a pinning effect [33].

More recently, Chen and colleagues demonstrated that an applied electric current (of ~50 A/cm^2) could enhance the grain boundary mobility (by >10 times) in the cathode side discontinuously in 8YSZ, leading to abnormal grain growth [34]. They attributed this effect to the accumulation of supersaturated oxygen vacancies on the cathode side that caused cation reduction to lower its migration barrier [34]. In this study, we have observed a somewhat opposite effect: discontinuous (abnormal) grain growth and/or coarsening in the anode side in ZnO during the flash sintering, which can be explained from the possible occurrence of an electric-potential-induced grain boundary (defect) structural transition by extending and combining Chen and colleagues’ concept (discussed above) [34], Tuller’s theory of grain boundary defect chemistry in ZnO [35], and the idea of grain boundary complexion transitions [36].

Most recently, flash sintering of nanocrystalline pure ZnO under AC fields between 0 and 160 V/cm was reported, where normal grain growth was observed [37]. In this study, we applied DC currents at a higher field of 300 V/cm to high-purity ZnO single crystals as well as pure and 0.5 mol.% Bi_2O_3-doped ZnO powder specimens. We have observed a number of interesting and intriguing phenomena, including the flash (thermal runaway) of ZnO single crystals, reduction of the onset flash temperature in powder specimens, anode-side abnormal grain growth (in contrast of the cathode-side abnormal grain growth reported for 8YSZ [34]), growth of aligned single-crystalline rods, and doping effects on deferring the onset flash sintering and homogenizing microstructures, which have greatly deepened and enriched our fundamental understanding of the sintering and microstructural development under electric currents. Moreover, a quantitative model has been developed for predicting the thermal runaway conditions that are in excellent corroboration with experimentally-observed onset flash temperatures, thereby suggesting that the flash (at least) starts as thermal runaway in ZnO based specimens.

2. Experimental

The pure and 0.5 mol.% Bi_2O_3-doped powder samples were fabricated by using purchased ZnO (Sigma Aldrich, St. Louis, Missouri, USA: >99.9% purity, <0.5 μm particle size) and Bi_2O_3 (Sigma Aldrich: ⩾99.8% purity, 90–210 nm particle size) powders. Nominally pure ZnO powders were ball milled with alumina media for 2 h in isopropyl alcohol with 0.5 wt.% of binder (10 wt.% of polyvinyl alcohol or PVA dissolved in isopropyl alcohol). 0.5 mol.% Bi_2O_3-doped ZnO powders were prepared by ball milling mixtures of the oxide powders and 0.5 wt.% of binder in isopropyl alcohol for 10 h. All powders were subsequently dried in an oven chamber at 80 °C for 12 h after milling. The 0.5 mol.% Bi_2O_3-doped ZnO powders were calcined at 600 °C for two hours in air in a covered Pt crucible, followed by another round of 2-h ball milling in isopropyl alcohol with 0.5 wt.% of binder and subsequent drying. Dried pure and 0.5 mol.% Bi_2O_3-doped ZnO powders were pulverized in a mortar and sieved under 150 mesh of sieve. The resultant granulated powders were uniaxially pressed at ~300 MPa in a mold (1/4 inch diameter) into green specimens (disks) with the approximate dimensions: D (diameter) = 6.4 mm and H (thickness) = 4 mm. The average bulk densities (±one standard deviations) of pure and 0.5 mol.% Bi_2O_3-doped ZnO green specimens were 63.5 ± 0.8% and 65.0 ± 2.2%, respectively, of the theoretical densities. The green specimens were then heated at the ramping rate of 5 °C per minute to 500 °C and baked at 500 °C isothermally for one hour to burn out the binders. After measuring the dimensions and weight of each sample, both sides of the specimen were pasted by Pt inks (Heraeus Inc, West Conshohocken, PA; catalog number: 116668009) with Pt wire buried underneath. The pasted specimens were then heated at the ramping rate of 20 °C per minute and baked at 500 °C for 20 min. This baking process was repeated approximately eight times (to attach Pt wires firmly without going to a higher baking temperature to avoid any shrinkage of ZnO specimens) until the Pt wire was connected solidly to the dried Pt pastes.

The electroded sample was placed close to the thermocouple within a tube furnace, with Pt wire connected to the power source. Each specimen was heated at the ramping rate of 5 °C per minute under an (initial) electric field at 300 V/cm (calculated based on the initial specimen thickness). Similar to a typical flash sintering experiment, the applied voltage was kept a constant until the resultant current reached a preset maximum value (I_{max} = 1 and 4 A, respectively, for this study), at which point the power source switched from the voltage-control mode to a current-limited mode. The maximum current densities and final electric fields in the activated state were estimated based on the actual measured dimensions of sintered specimens listed in Table 1, along with other experimental conditions and results. When the power density reached the maximum, the electric power source was kept on for an additional 30 s, with furnace being turned off (the furnace