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FAST/SPS sintering of nanocrystalline zinc oxide—Part II: Abnormal grain growth, texture and grain anisotropy

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ABSTRACT

This second part describes the retention of nanocrystallinity during sintering of ZnO by means of Field-assisted Sintering Technique/Spark-Plasma-Sintering (FAST/SPS), whereas the first part [doi: 10.1016/j.jeurceramsoc.2015.12.009] concentrated on hydroxide-ion-enhanced densification and defect stoichiometry. Interface design by surface bound water on zinc oxide offers a novel method to control in a new way diffusion in nanocrystalline polycrystals. Therefore, zinc oxide powder was humidified or dried and afterwards heated quickly (100 K/min) by FAST/SPS. Interestingly, the densification is strongly promoted in presence of water reducing the sintering temperature to 400 °C. Thus, grain growth is decreased by one order of magnitude while achieving full densification. The crystalline texture developed irrespective of temperature or presence of water. Moreover, the formation of hydroxide complexion at grain boundaries is discussed as it might modify grain boundary mobility and lead to pronounced grain anisotropy perpendicular to the uniaxial applied load.

1. Introduction

Since the majority of physical properties are affected by the residual porosity of the material, it is essential to obtain nearly full densification. Indeed, the sintering of nanocrystalline dense bulk materials with grain sizes below 100 nm is still a challenging task [1]. In general, the retention of nanocrystallinity depends on the competition between densification and grain growth, which driving forces both depend on reciprocal grain size [2,3]. Typically, grain growth is suppressed by the application of an external pressure [4], grain boundary pinning (addition of a second phase/doping), very high heating rates [5–7] or two-step sintering [4,8]. Nevertheless, extensive coarsening takes place for sintering of pure ZnO, resulting into either significant residual porosity [9] or large grain size of microns [4,10]. Moreover, grain boundary mobility is decreased by a large amount of small pores, resulting into a pinning force on the boundary. Increasing particle agglomeration will raise the mean pore size due to the formation of intra-agglomerate pores, while decreasing the relative amount of pores at grain boundaries [11,12]. Thus, the retention of nanocrystallinity also depends on a high green density and homogeneity of the material [2,3]. In this context it is worth to mention that dry molding of powders is typically restricted to 50–61%TD [4–14], but aqueous casting, e.g., pressure filtration [8], offers much higher green density by benefiting from reduced friction between particles and prevent large agglomerates [2,15]. Moreover, water is typically chemically adsorbed by the oxide surface and forms hydrated interface [16]. Recently, Quach et al. [17] suggested that driving forces for grain coarsening are decreased by the adsorption of hydroxides onto the oxide surface due to a reduction of surface energy. In order to achieve temperatures while water is still participating at densification process, high heating rates are required. These high heating rates (>100 K/min) can be achieved by Field-Assisted Sintering Technology (FAST), which is also referred to as Spark-Plasma-Sintering (SPS) [18]. The present study will highlight the influence on adsorbed water on the microstructural development of nanocrystalline zinc oxide. Interestingly, the presence of adsorbed water on nanocrystalline ZnO strongly promotes diffusion resulting into significant decrease of sintering temperatures necessary for full densification, which offers a reduction of grain boundary mobility [19]. Furthermore, the growth of polycrystalline microstructure may result in the for-

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mation of texture, which affects electrical [20–23] and mechanical [24] properties. In general, texture is a preferred alignment of grains or crystallographic axis [22], but crystalline texture and morphologic texture (anisotropy of grain shape) do not necessarily need to coincide [23]. Indeed, the formation of texture during coarsening is promoted by anisotropy of surface energy. ZnO exhibits a higher surface energy for (0 0 0 2) plane compared to $(1\,0\,\bar{1}\,0)$ or $(1\,0\,\bar{2}\,0)$ planes, due to its polar crystal structure [25–27]. It is noteworthy that Dillon and Harmer [28,29] investigated characteristic structure and composition at grain boundaries. These so called complexions at grain boundaries exhibit characteristic grain boundary mobility [30]. Moreover, different types of complexions can co-exist and modify the grain boundary mobility of specific grains, which delivers a reasonable explanation for abnormal grain growth [31]. Therefore, investigations on interface engineering e.g., by complexions is declared to provide one of the most interesting challenges for ceramic research for the next decade [32].

Moreover, ZnO is known for preferred growth direction along the polar *c*-axis of the crystal lattice offering rod-like particles [33–35] or structured thin films [36]. However, countless sintering studies of pure ZnO showed that polyhedral grains with quasi globular shape always result from isotropic (spherical) powder particles [4,10,37–42]. This isotropic morphology was found to be independent from sintering process (free sintering, hot pressing, FAST/SPS) or initial particle size (nano to macro scale). In contrast, anisotropic grain growth for polycrystalline ZnO is known to occur only for sintering of powders which originally contain a certain fraction of non-spherical particles [43]. Here, for pure ZnO no study exists that reports the development of grain anisotropy from isometric powder particles. From the application point of view a texture will affect the electrical [20] and optical [44] properties, whereas anisotropy of electrical properties seems promising for ceramic in electric industry [20,23].

While part I [19] concentrated on the effect of surface bound water on the densification behavior and defect stoichiometry, the current part II highlights the microstructural development of hydroxide doped ZnO during sintering.

2. Experimental procedure

2.1. Materials and methods

The standard ZnO powder utilized for the experiments is referred as NG20 (Nanogate AG, Quierschied- Göttelborn, Germany). The NG20 data sheet announces a purity of >99.99 wt% and a primary particle size of 20–50 nm. The as received zinc oxide powder was either humidified or dried directly before sintering in order to investigate the effect of bound water on the microstructural behavior. For that purpose, a total amount of 3 g zinc oxide powder was stored in a glass beaker inside an environmental chamber (KBF 240, Binder GmbH, Tuttlingen, Germany) at 20 °C with 14 g/m^3 of moisture or the powder was dried in a drying cabinet at 120 °C with «0.5 g/m^3 («0.1% relative humidity). Afterwards, the stored powder was directly purred inside a FAST/SPS graphite die with an inner diameter of 20 mm and further precompacted for 1 min at 50 MPa by uniaxial pressing. The sintering study of nanocrystalline ZnO is mainly focusing on sintering by a FAST/SPS device (HP-D5, FCT Systeme, Rauenstein, Germany). The inner part of the graphite die (type 2233, Mersen, Paris, French) and the graphite punches were covered with a 0.4 mm thick graphite sheet in order to improve electrical contact and to prevent reaction between the compact and the tool. Moreover, a low density graphite dumping covered the graphite die to reduce the thermal gradient during sintering. The sintering chamber was evacuated to 1 mbar, flushed with pure Argon (99.999% purity) and evacuated again before the start of the temperature schedule in order to remove the residual foreign gas species. The sintering conditions were set with an external pressure of 50 MPa, 100 K/min heating rate and maximum sintering temperatures of 400 °C and 800 °C under aqueous and dry conditions, respectively. The temperature measurement and control was performed with a type K thermocouple, which was placed in a radial hole at a distance of 5 mm to the ZnO body. The pulsing pattern of the electric current was set to 25 msec: 5 msec (on: off). Moreover, the relative sintering density could be determined as a function of temperature and processing time by measurement of the axial displacement, as sintering geometry is constrained in radial direction due to the die and shrinkage could only occur in axial direction. Therefore, thermal and mechanical expansion/compression had to be considered by correcting the measured displacement by the same thermal and compressive schedule with a fully densified specimen. Here, accuracy of displacement measurement is ±10 μm. In addition, single experiments were performed with electrically insulation of the ceramic body, in order to investigate the effect of electrical current on grain growth behavior. Therefore, the tool setup was modified by installing alumina discs (Rubalit 710 Alumina, CeramTec GmbH, Plochingen, Germany) between NG20 body and graphite punches. For the insulating alumina discs the data sheet of the producer announces an electrical resistance of 10^{13} Ωcm and 10^{9} Ωcm at 25 °C and 900 °C, respectively.

2.2. Microstructural characterization

The microstructural analysis on sintered ZnO specimen (only NG20) focused on two aspects: grain shape and crystalline orientation. Sintered disc specimens were cut in bar geometry (18 mm × 1.5 mm × 1.5 mm), which allowed to evaluate microstructural features parallel and perpendicular to uniaxial applied pressure, which are further referred to *z*- (axial) and *x*, *y*-directions (radial), respectively. The bars were grinded with SiC paper and finally mirror polished using diamond paste (MasterPolish, Buehler, Minnesota, USA). Transmission electron microscopy (TEM, JEM-3010 JEOL Ltd., Tokyo, Japan) and high-resolution scanning electron microscopy (HRSEM, Auriga60, Carl Zeiss AG, Oberkochen, Germany) were performed in order to evaluate size distribution and orientation of grains and pores. The grain size measurement was carried out on polished samples using the line interception method with the software Lince (v. 2.31, Ceramics Group, TU Darmstadt) using a factor of 1.56 [45], evaluating at least 300 grains in different micrographs. In addition, grain size and shape were evaluated by means of ImageJ software (v1.45s, National Institute of Health, USA) applying threshold value method at 1000–1400 grains per distribution. For shape evaluation, each grain was fitted by ellipses of the same orientation, area and ratio of length to width, which enables to determine the aspect ratio and the orientation angle (α) referring to specimen geometry. High resolution transmission electron microscopy (HRTEM) was performed with a field emission transmission electron microscope (JEM2100F, JEOL Ltd., Tokyo, Japan).

Secondly, crystalline texture was investigated by electron beam scattering diffraction (EBSD) and X-ray diffraction (XRD) by means of Rietveld refinement. The crystallographic phase of sintered specimen was characterized by means of X-ray diffraction (XRD). XRD measurements were carried out using a D8-Discover (Bruker AXS, Billerica, USA) with Cu-Kα radiation at λ = 1.54056 Å, operated at 40 kV and 40 mA, a step size of 0.02° and a counting time of 1.6 s. Furthermore, the crystallite size was also determined by means of Scherrer analysis for partially sintered specimen, which showed a crystal size smaller than 100 nm by SEM. Here, the $(1\,0\,\bar{1}\,0)$, $(1\,0\,\bar{2}\,0)$ and (0 0 0 2) Bragg peaks were fit with the Pseudeo-Voigt function, a shape factor $K = 0.94$ was applied to Scherrer equation [46] and