Research Article

Microstructure and Density of Sintered ZnO Ceramics Prepared by Magnetic Pulsed Compaction

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Three different sintered ZnO ceramics were prepared by magnetic pulsed compaction (MPC) and other conventional methods. The microstructures of the sintered ZnO ceramics prepared by MPC at sintering temperatures ranging from 900 to 1300°C showed a homogeneous grain growth compared to those of the samples prepared using other methods under the same sintering conditions. This implies that interpowders and/or intergrains can induce the minimization of wall friction effect because of the application of a high compaction pressure for a short process time in the MPC method. In addition, the microstructure of the sample obtained using the cold isostatic pressing method showed the presence of heterogeneous regions, indicating its low quality even though the densities of the three different samples were almost similar in the range of 97–99% at sintering temperatures of 900, 1100, and 1300°C. Therefore, different methods used for the compaction of ZnO ceramics may result in different microstructural and physical properties of the product.

1. Introduction

Recently, ZnO has attracted increasing attention in various research areas, such as solar cells, transparent electrodes, varistors, gas sensors, and piezoelectric devices [1–4]. This is because ZnO exhibits high transmittance in the visible region, and its electrical resistivity can be easily controlled by doping with elements such as Al [5–8] and Ga [9–11]. ZnO is also advantageous from the economic and the environmental viewpoints owing to its low cost and nontoxic properties [12–14]. However, most of the recent studies are focused on low-dimensional ZnO nanostructures because the 0- and 1-dimensional nanoscale is relatively free from electric and magnetic barriers, and consequently, they exhibit diverse and complicated functions when compared to the bulk materials. In other words, studies on the comparison of sintered ZnO bulk ceramics prepared using different synthetic methods are very scarce because of the time-consuming multimanipulations. Most importantly, the sintered ZnO ceramics should exhibit high relative density and microstructural homogeneity to ensure the reliability of

the product. Sintered ZnO ceramics are generally prepared via a series of optimization processes consisting of compacting, sintering, and thin-film deposition. Among these steps, the compacting process is the most critical because the physical properties of the compact mainly determine the final optical and electrical properties of the prepared ZnO samples. For instance, at the first stage, if there are defects in a compact or the microstructure is not uniform, they critically affect the subsequent processes. Therefore, detailed analyses are required to synthesize high-quality compacts and to understand the effects of compacting conditions on the physical properties of the sintered ZnO ceramics [15–19]. In this study, three different compacting methods, namely, (1) conventional uniaxial pressing, (2) cold isostatic pressing (CIP), and (3) magnetic pulsed compaction (MPC), were used for fabricating high-quality sintered ZnO ceramics, and the properties of the three different samples were compared. In particular, the MPC technique is more advantageous than other methods because an extremely high pressure (~5 GPa) can be applied to the powders within a short period of time (~500 μ s) [20]. The physical properties of the ZnO ceramics,

including green and relative densities corresponding to the functional and microstructural changes in the samples, were evaluated. The comparative results were used to establish the effect of compacting conditions on the properties of the sintered ZnO ceramics.

2. Materials and Methods

The ZnO raw powders (99.9% purity) used in the three different synthetic methods were purchased from Kojundo Chemical Laboratory, Japan. The average particle size of the ZnO raw powder was approximately $3.285\ \mu\text{m}$. Polyvinyl alcohol (OCI, Korea) used as a binder for the ZnO powder was mixed with distilled water. Then, the mixture of the slurry binder and the ZnO powder was completely dried to obtain bulk ZnO.

2.1. Compacting Methods. The three different compacting methods used for preparing the sintered ZnO ceramics are described as follows:

- (1) In uniaxial pressing, the ZnO powders were pressed into a steel mold after lubricating the inside of the steel mold with a BN spray for easy detachment of the ZnO ceramics from the steel mold. The mold diameter was 20 mm, and the maximum pressure used for compacting ZnO was 165 MPa, which was applied for 1 min.
- (2) In CIP, the ZnO powders were compacted under a pressure of 180 MPa for 10 min after uniaxial pressing at 119 MPa for 1 min.
- (3) In MPC, the ZnO powders were compacted by MPC uniaxial pressing at 800 MPa for approximately $500\ \mu\text{s}$. The notable feature of the MPC method is that the applied pressure and time are much higher and shorter, respectively, than those of the uniaxial pressing and the CIP methods. Table 1 presents the details of the compacting conditions, such as mass, lubrication condition, diameter, pressure, and time used for the different methods.

2.2. Sintering. All the specimens were preheated at 400°C for 1 h in air to burn off the binder from the ZnO samples. Then, continuous sintering was performed at 900, 1100, and 1300°C for 1, 2, and 4 h without the use of supporting gases, respectively. The heating rate for all the samples was set at $5^\circ\text{C}\cdot\text{min}^{-1}$. After the sintering process, the samples were cooled in the furnace.

2.3. Characterization. The green densities and the relative densities of the cylindrical ZnO samples were calculated from the weight to volume ratio. Furthermore, while calculating the relative density, Archimedes' principle was applied using distilled water for factual accuracy. For studying the microstructural properties, all the sintered samples were gradually polished with SiC paper and $1\ \mu\text{m}$ diamond paste. Subsequently, the smooth surfaces of the

TABLE 1: Compacting conditions used for uniaxial pressing (Uni), cold isostatic pressing (CIP), and magnetic pulsed compaction (MPC) processes.

Compact mass	11.22 g	
Lubrication condition	BN sprayed	
Mold diameter	Uni MPC	20 mm
Compacting pressure	Uni CIP (Uni) MPC	165 MPa 180 (119) MPa 800 MPa
Compacting time	Uni CIP MPC	1 min 10 min $\sim 500\ \mu\text{s}$

FIGURE 1: Variations in the green densities of the ZnO ceramics prepared using the three compacting methods (uniaxial pressing, CIP, and MPC) with respect to the sintering temperature and duration.

specimens were etched with hydrochloric acid for 30 s. The microstructural observations of parallel and perpendicular cross sections were performed using a Keyence VHX-900 optical microscope and a Hitachi S-4300SE scanning electron microscope. The mean grain sizes were measured using the image analysis software.

3. Results and Discussion

3.1. Compacting Properties. Figure 1 shows the comparison of the green densities of the ZnO compacts prepared by the three compacting methods. The green densities of the samples prepared using the different methods are approximately in the range of 60 to 68%. It appears that there was no significant difference in the value of green density even though the compacting pressure used in MPC was 4.8 times larger than the compacting pressure used in uniaxial pressing (Table 1). The green density of the uniaxially pressed compacts was 62.6%, and that of the CIP compacts with uniaxial pressing was 64.9%. The maximum green density of 66.5% was obtained using the MPC method. Based on this result, we surmise that the relationship between the

compacting pressure and the green density is not linear. In addition, it also seems to be converging to a certain maximum value. Nevertheless, it is important to determine the best method among the three because the green density can generally affect the final relative density at the same sintering conditions [21].

3.2. Sintering Properties. The relative densities of the three different ZnO ceramics sintered at different temperatures and durations are shown in Figure 2. The densities of all the sintered ZnO ceramics increased with increase in the sintering temperature. This is correlated with the number, and the size of pores decreases as the sintering temperature increases [22]. For example, the samples compacted by the three different methods exhibited densities greater than 97, 98, and 99%, at 900, 1100, and 1300°C, respectively. However, the relative density values of the samples compacted using the MPC method at 1300°C were slightly lower than those of the samples compacted using the uniaxial pressing and CIP methods. While the effect of sintering temperature on the relative density of the compacted sample is consistent, there is no direct relationship between the sintering time and the density except for samples compacted using MPC, as can be seen from Figure 2. This is in contrast to a previous report, in which the relative density of ZnO ceramics was found to be dependent on sintering time in the isothermal sintering test [23]. Therefore, the inconsistent results related to the sintering time observed in the present study can be associated with the nonisothermal sintering test arising from the densification and the consequent grain growth phenomena during the sintering processes.

3.3. Microstructural Properties. Figure 3 shows the variations in the grain sizes of the different sintered ZnO ceramics. At 900°C, no grain growth was observed regardless of the compacting method and the sintering time. Only the densification phenomena occurred because the supplied thermal energy at 900°C was not sufficient for atomic diffusion from one site to the other. However, at 1100 and 1300°C, notable grain growth occurred, and the grain size increased with increase in the temperature. The accelerating tendency of the grain growth was more evident in the samples compacted using the MPC method. In other words, the grain size of the sintered ZnO ceramics prepared using the MPC method was larger than that of the samples prepared using the other compacting methods at the same sintering conditions. However, Ahn et al. [24] studied the effects of green density on grain growth and reported that a high green density can suppress the grain growth during sintering. Therefore, the unusual trend in the grain growth observed in the samples prepared using the MPC method is believed to be caused by the aggregation of minute amounts of grains with sizes smaller than the critical grain size.

Figures 4 and 5 show the results of microstructural observations at the central (marked as (a)) and the outer (marked as (b)) regions of the parallel and the perpendicular cross sections of the samples prepared by CIP (Figure 4) and

FIGURE 2: Variations in the relative densities of the sintered ZnO ceramics prepared using the three compacting methods (uniaxial pressing, CIP, and MPC) with respect to the sintering temperature and duration.

FIGURE 3: Variations in the grain sizes of the sintered ZnO ceramics prepared using the three compacting methods (uniaxial pressing, CIP, and MPC) with respect to the sintering temperature and duration.

MPC (Figure 5), respectively. The sintered ZnO ceramics synthesized using the CIP method showed a significant difference in the grain size at the center and the outer regions irrespective of the direction of the cross section. In other words, the grain size and the density at the central region of the ZnO ceramics compacted using the CIP method are

FIGURE 4: Perpendicular and parallel cross-sectional microstructures of the ZnO ceramics compacted by uniaxial pressing and CIP and sintered at 1300°C for 2 h recorded from (a) central region and (b) outer region.

FIGURE 5: Perpendicular and parallel cross-sectional microstructures of the ZnO ceramics compacted by MPC and sintered at 1300°C for 2 h recorded from (a) central region and (b) outer region.

slightly smaller and higher, respectively, than those at the outer region (Figure 4). However, the sintered ZnO ceramics compacted using the MPC method showed a similar grain size and density at the central and the outer regions. This indicates increased grain growth and more homogeneous

grain size distribution in the sintered ZnO ceramics compacted using the MPC method than the samples prepared using the other compacting methods at the same sintering conditions. The grain size distributions of all the samples are given in Table 2.

TABLE 2: Comparison of the grain sizes of the central and outer regions in the sintered specimens prepared using the three compacting methods (uniaxial pressing, CIP, and MPC).

Sintering temperature (°C)	Compacting method	Grain size (μm)					
		1 h		2 h		4 h	
		Center	Side	Center	Side	Center	Side
900	Uni CIP MPC	3.285 (no grain growth)					
1100	Uni	6.66	17.66	6.34	18.47	7.31	17.39
	CIP	7.97	16.42	9.59	17.97	11.64	19.41
	MPC	14.44	16.76	15.13	19.03	14.06	23.50
1300	Uni	10.98	18.21	10.85	20.27	11.46	25.89
	CIP	9.02	18.85	12.65	23.00	11.94	24.71
	MPC	26.94	29.29	24.71	37.37	24.29	34.29

FIGURE 6: Perpendicular and parallel cross-sectional microstructures of the ZnO ceramics compacted by MPC and sintered at 1300°C for 2 h recorded from (a) central region and (b) outer region.

The microstructures of the sintered ZnO sample prepared by uniaxial pressing and CIP at 1300°C are presented in Figure 6. Compared with normal microstructures, two specialized regions existed: one corresponding to abnormal grain growth (Figure 6(a)) and the other corresponding to grain size transition (Figure 6(b)). The abnormal grain growth was not observed in the sintered ZnO ceramics prepared using the MPC method, whereas it was observed in the samples prepared by uniaxial pressing and CIP as shown in Figure 6(a). Furthermore, the grain size transition region was observed in the samples prepared by uniaxial pressing and CIP at 1300°C, while it did not exist in the sample prepared using the MPC method (Figure 6(b)). The main cause for the abnormal grain growth and the grain size transition is probably the relative density inhomogeneity arising from the friction between the mold wall and the ZnO powders during the compaction process as it has been reported previously [25, 26].

Figure 7 shows the effect of relative density inhomogeneity on the microstructure of ZnO samples prepared by uniaxial pressing and CIP. The grain growth tendency at the outer region is gradually increased because of its higher relative density. On the other hand, the onset of grain growth at the center is delayed. Owing to the instability arising from the differences in the grain growth at different regions, the region of abnormal grain growth was observed only at the

FIGURE 7: Schematic diagram of the sintered ZnO ceramic compacted by uniaxial pressing and CIP.

center. However, the grain size homogeneity observed in the MPC method is attributed to the high compacting pressure (800 MPa) applied for an extremely short period of time ($\sim 500 \mu\text{s}$). In short, the MPC method minimizes the effects of wall friction that causes nonuniformity in the grain size.

4. Conclusions

In this study, pure ZnO ceramics were compacted by MPC, and their physical properties such as green and relative densities and the microstructure were compared with those of the ZnO samples compacted by uniaxial pressing and CIP. The following conclusions were drawn from the experimental results:

- (1) The green density of the MPC compacts was 66.5%, which is the highest value when compared to the densities of the samples prepared by uniaxial pressing (65.6%) and CIP (64.9%). The relative density was greater than 97, 98, and 99%, respectively, at 900, 1100, and 1300°C regardless of the compacting methods.
- (2) The grain growth tendency of the sintered ZnO ceramics increased with increase in the temperature from 1100 to 1300°C. This is attributed to the aggregation of minute amounts of grains with sizes smaller than the critical grain size.
- (3) The sintered ZnO ceramics compacted using the MPC method showed a homogeneous grain size at the inner and outer regions of the samples without the formation of abnormal grain growth and grain size transition regions. The MPC method can be used to achieve microstructural homogeneity because of the application of a high compacting pressure (800 MPa) for an extremely short period of time ($\sim 500 \mu\text{s}$).

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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