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Hot pressing of nanocrystalline zinc oxide compacts: Densification and grain growth during sintering

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Abstract

Sintering behavior of nanocrystalline zinc oxide (ZnO) powder compacts using hot pressing method was investigated. The sintering conditions (temperature and total time) and results (density and grain size) of two-step sintering (TSS), conventional sintering (CS) and hot pressing (HP) methods were compared. The HP technique versus CS was shown to be a superior method to obtain higher final density (99%), lower sintering temperature, shorter total sintering time and rather fine grain size. The maximum density achieved via HP, TSS and CS methods were 99%, 98.3% and 97%, respectively. The final grain size of samples obtained by HP was greater than that of TSS method. However, the ultra-prolonged sintering total time and the lower final density (88 ks and 98.3%) are the drawbacks of TSS in comparison with the faster HP (17 ks and 99%) method.

Keywords: A. Hot press; A. Grain growth; D. ZnO; Densification

1. Introduction

Nanocrystalline materials have received a great deal of attention over the last years. These materials are potentially attractive for many applications since the reduction of the grain size to the nanometer scale can improve their physical and mechanical properties [1–3].

Zinc oxide (ZnO) is one of the most important multi-functional materials, which can be used in many fields, such as optoelectronic devices, gas sensors, solar cells and varistors [4–7]. It was found that the physical properties of ZnO are directly contributed by the grain size. For instance, Duran et al. [1] have also, reported that ZnO with a smaller grain size can exhibit larger breakdown voltages. The grain size reduction is, additionally, exposed to enhance the conduction nonlinearity [8]. Besides, Wang and Gao [2] recently reported the optical and electrical properties of ZnO to be strongly depended on the volume of grain boundaries. Therefore, it is of the great significance to control the grain size of ZnO compacts thorough the sintering procedure. However, manufacturing of dense ZnO samples with a fine microstructure using traditional forming techniques followed by pressureless sintering has not proven easy. Roy et al. [9], For example, sintered ZnO nanopowders (30 nm) at 900 °C for 6 h and reported the relative final density of 99% TD, while the final grain size was around 2 μm.

There have been always three main approaches, usually applied to avoid the accelerated grain growth associated with densification and, therefore, provide fine microstructures. The first one is the addition of second phase particles (dopants) to modify diffusion processes, prevent the grain boundary migration and, hence, suppress the grain growth. Nevertheless, the second phase can be destructive to densification and physical behavior. Han et al. [10] have, for instance, shown that, while the addition of Al significantly inhibits the grain growth of ZnO and increases the grain growth kinetic exponent from 3 to 6 for pure and Al-doped ZnO, respectively, the ZnO system s a notable decline in the densification rate. Sedky et al. [11] have studied the sintering behavior of Fe-doped ZnO samples. They have reported that in spite of the grain growth suppression caused by the Fe content, the abovementioned approach diminishes final density of the sintered specimens. On the other hand, their investigation exposed the detrimental effect of Fe dopants on the electrical conductivity of pure ZnO samples.

The second approach is a new technique called two-step sintering (TSS). This method offers a promising approach for

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fabrication of bulk nanograin ceramics, thereby, exploiting the difference in kinetics between grain boundary diffusion and grain boundary migration [12,13]. TSS is carried out by the high temperature firing followed by rapid cooling and low temperature holding of the samples. Using two-step sintering method, the authors managed to manufacture submicrometer grained ZnO bodies for the first time in their previous work [14].

The third is the use of particular consolidation techniques, such as hot pressing or spark plasma sintering. The application of an external pressure increases the driving force for densification. Hot pressing provides one of the most reliable techniques to adjust the relative rates of densification [15,16].

According to the best knowledge of the authors, few reports are available in the literature talking over the densification and grain growth, during hot pressing of nanocrystalline ZnO samples. Hynes et al. [17] hot-pressed nanophase ZnO compacts (at 60 MPa and 550 °C for 30 min) to obtain bodies with the relative density of 95% TD. But, they have not any clear report on densification and grain growth during hot pressing method. In the present work, the densification and microstructural evolution of samples during hot pressing were investigated. The sintering conditions (such as total time and temperature of sintering) and results (final density and grain size) of HP, CS and TSS methods were compared.

2. Experimental procedure

2.1. Materials and methods

Zinc oxide nanopowder (purity of the powder was higher than 99.7), used in this study, was supplied from Inframat Advanced Materials (Farmington, CT, USA). The powder was hot pressed at the pressure of 50 MPa using cylindrical graphite dies coated with boron nitride with an inner diameter of 10 mm. The sintering temperature varied from 400 to 850 °C with interval of 50 °C. The heating rate was adjusted at 0.05 °C s^{-1}. After heating to maximum temperature, the specimens were held at this temperature for 1 min, so as to yield a homogenous temperature in the whole body of samples.

To obtain green bodies for CS and TSS experiments, the powder was uniaxially cold pressed at 200 MPa into pellets with diameter of 10.2 mm and thickness of 3 mm. Based on the ZnO theoretical density (TD) (5.606 g cm^{-3}), the average green density of the nanocrystalline ZnO powder compacts was determined to be ~0.61 TD after pressing.

Conventional sintering was performed in a muffle laboratory furnace. The sintering was carried out between 600 and 1200 °C. The sintering conditions (heating rate and holding at maximum temperature) were chosen same as the HP method. Sintering of the green bodies is operated under the conditions of TSS procedure which was discovered as the optimum TSS regime in the previous work of the authors [14].

2.2. Characterization

The morphology of the powder was examined by transmission electron microscopy (TEM, Philips, CM200 FEG, the Netherlands). Densities of sintered samples were measured by the Archimedes method with distilled water. The outermost layer of hot-pressed ZnO was removed by mechanical polishing before the density measurements. For investigating the microstructural evolution, sintered pellets were fractured and then studied using scanning electron microscopy (SEM, Philips XL30, the Netherlands). An image analyzer calculated the mean grain size of the samples. To determine the average density and grain size of the specimens in all tests, at least three samples were used for each experiment.

3. Results and discussion

Fig. 1 represents TEM micrographs of the nanocrystalline ZnO powder. It can be observed that particles are mainly rounded shape and the particle size ranges from 20 to 40 nm. According to the information given by the supplier, the specific surface area of the powder determined by Brunauer–Emmett–Teller (BET) method was 35 g cm^{-3}. The particle size, determined by the TEM observation, is in a good agreement with the average particle size, calculated from the BET result (~31 nm).

Fig. 2 shows the variation of density and grain size of hot-pressed nanocrystalline ZnO versus sintering temperatures. As shown in this figure, the sintering plot exhibits a sigmoidal shape. The densification starts at around 450 °C and the densification rate increases dramatically with the temperature rise up 600 °C. It can be seen that a 200 °C increase (from 500 to 700 °C) in temperature results in the fractional density evolution from ~0.65 to ~0.95. The specimens with the relatively full density of 99% TD are produced by hot pressing at 850 °C. As can be seen, the grain size of ZnO samples increases with the temperature and the rate of grain growth shows a significant improvement at temperatures higher than 650 °C. The dense ZnO samples, sintered at 850 °C, have microstructures with the mean grain size of about 1.4 μm. From the above experimental results and analysis, it can be found that despite improving the sample density, an increase in the sintering temperature increases the grain size. Employing the

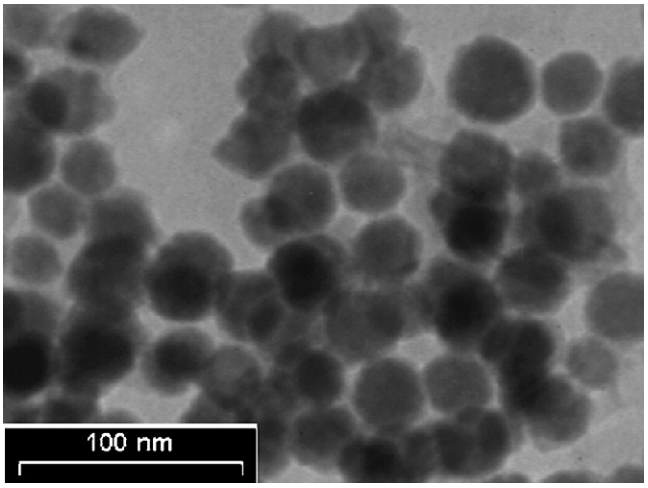

Fig. 1. TEM micrograph of the as-received nanocrystalline ZnO powder.

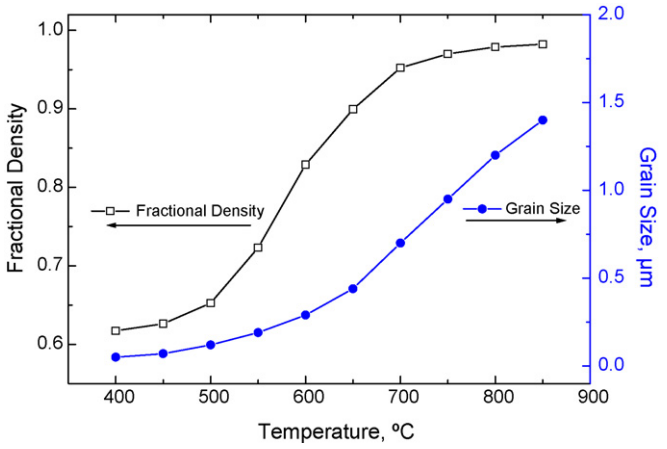

Fig. 2. Fractional density and grain size of hot-pressed nanocrystalline ZnO under 50 MPa vs. temperature.

pressure thorough the sintering procedure is not only helpful to remove the porosities from the powder compacts but also provides an additional driving force for densification and, hence, yields full dense samples (99% of TD).

Final densities achieved by hot pressing and conventional sintering are displayed in Fig. 3 as a function of temperature. As shown in this figure, CS, generally, results to the significantly lower densities than HP at equivalent temperatures, and the densification starts ~200 °C earlier when the pressure is applied during the HP.

In order to have an accurate comparison between TSS, HP and CS methods, results concerning with the sintering path (grain size versus fractional density) as well as the SEM micrographs (Fig. 5(a–c)) of near full dense samples are presented in Figs. 4 and 5, respectively.

The results (Fig. 4) indicate that, no matter both methods of CS and HP show the parabolic growth in the sintering final stage (fractional density >90%), the grain growth tends to follow a moderate trend during the HP (Fig. 5(b)), in comparison with CS (Fig. 5(c)). In contrast, the results of TSS method demonstrate no trace of the triggered growth, even, in the final stage of sintering (Fig. 5(a)).

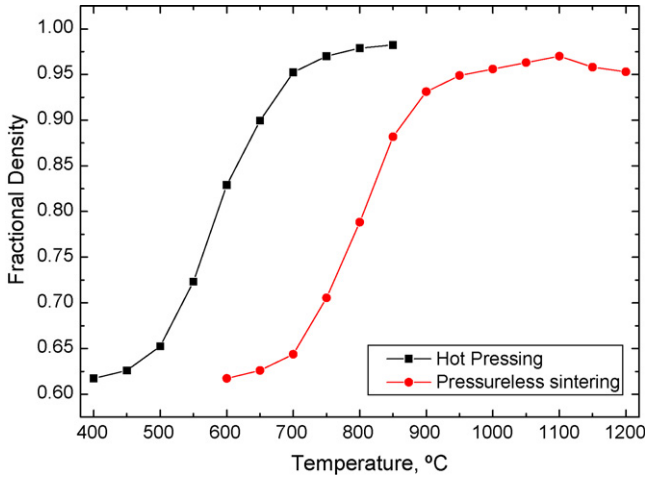

Fig. 3. Fractional density of hot-pressed and conventionally sintered nanocrystalline ZnO compacts vs. temperature.

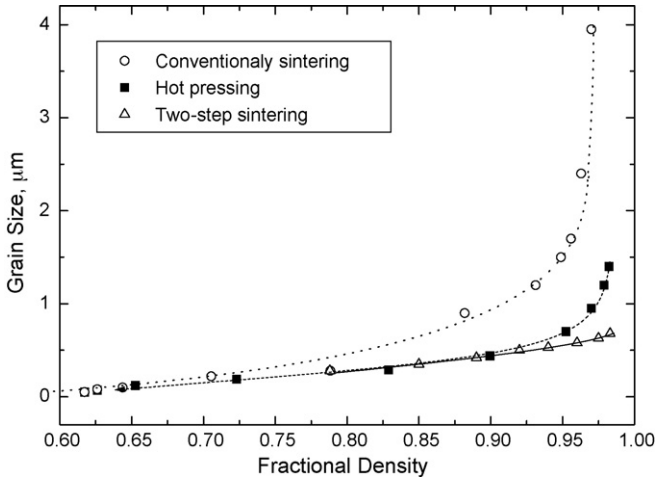

Fig. 4. Sintering path (grain size/fractional density) for sintered nanocrystalline ZnO compacts by three different methods.

The fact is that the grain growth is not directly contributed by the applied pressure. The effect of an external pressure, therefore, becomes more obvious in the system when the grain growth rate relative to the densification rate is high (for example, in the sintering final stage of CS (Fig. 4)). Since the application of an external pressure in the system increases the densification rate, it leads to a reduction of sintering temperature (Fig. 3) and consequently, the further grain growth suppression (Fig. 4). As presented in many pervious publications [13–15], the TSS method is naturally a favorable method to control the grain growth during densification in the final stage of sintering. The lower sintering temperature (T_2) in the TSS second step is the parameter to account for decent grain growth suppression provided by this method. The immobile triple point junctions, at this low temperature (T_2), can suppress the grain boundaries as the major motivator of the grain growth, while the grain boundary diffusion is still active to obtain near full dense samples (detail of TSS condition for nanocrystalline ZnO is available in [14]).

On the other hand, Fig. 4 shows the capability of HP to produce the specimens with higher density (99%) than CS (97%) and TSS (98.3%) methods. In the case of ZnO nanoparitcles, two significant problems are likely to happen at higher temperatures (>1000 °C) that retard the densification around 97% TD. The first problem is aroused by the insoluble gas entrapped in the pores [17]. Mazaheri et al. [14], have, for instance, shown that in higher temperatures than 1100 °C (in the case of nanocrystalline ZnO), an increase in the gas pressure entrapped in the pores may prohibit the mass transport caused by the diffusion mechanisms. The second problem is the material loss (including zinc and oxygen) from the surface of the powder to the furnace wall that results to a decrease in the final density at higher temperatures. There are also some investigations in the literature that prove the dramatic weight loss above 1100 °C, using thermogravimetric analysis (TGA) [14,17]. Thus, the density increase from 1100 to 1200 °C, not only results in the exaggerated grain growth but also reduces the final density (see Fig. 3). Meanwhile, as the HP declines the

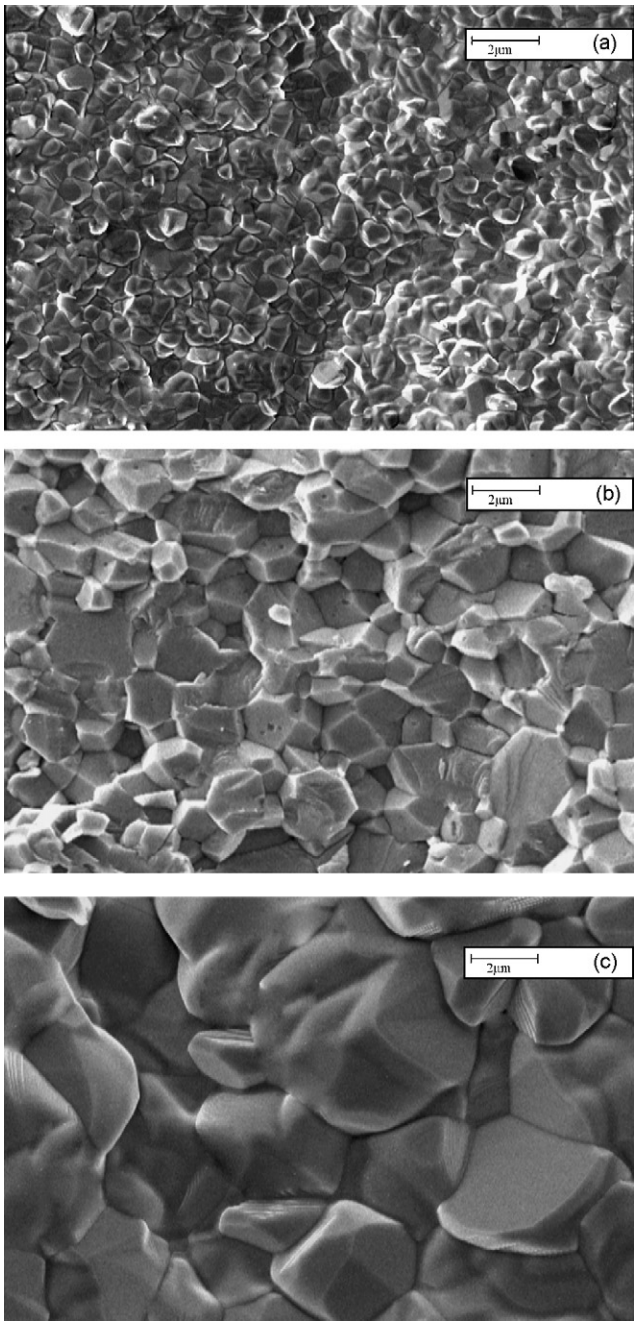

Fig. 5. SEM micrograph of near full dense samples sintered under TSS (a), HP (b) and CS (c).

sintering temperature, the mentioned problems are removed as a result of applying this method. The lower sintering temperature in the HP also, results in a lower pressure of insoluble gas. On the other hand, applied pressure during the HP method, can act as an opponent factor against gas pressure. Thus, the porosity can collapse easier than in the CS method. Besides, in the case of CS, when the pressure of entrapped gas becomes equal to the capillary pressure of the pore, the pore stops shrinkage and the maximum attainable sintered density is reached. Application of an external pressure after the pore isolation can, hence, increase the sintered density up to a higher value than that by the CS method. Additionally, according to

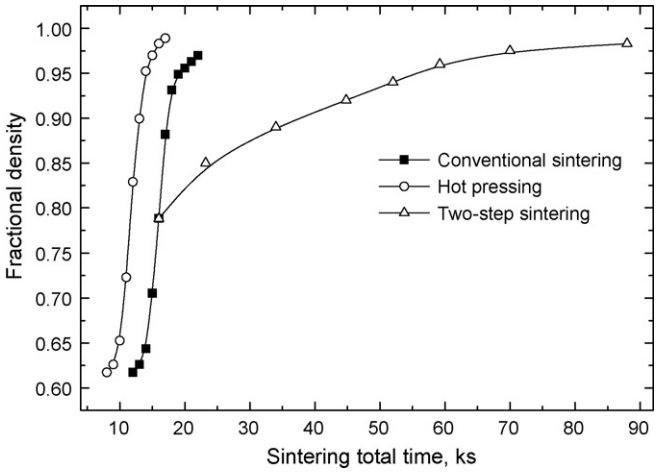

Fig. 6. Fractional density of samples sintered using three different methods vs. total time of sintering.

the TGA results [14], at the hot pressing temperatures of <850 °C, the material loss from surface of the particle was not observed.

Fig. 6 shows the fractional density of samples sintered via three different methods versus the total time of sintering. Although, the two-step sintered specimens have smaller grains than the hot-pressed bodies (see Fig. 5), the ultra-prolonged sintering time of TSS method as well as the lower density of the specimens have set severe restrictions on the technological application of this method (see Fig. 6). The HP is, therefore, an efficient method to remove the problems that many other sintering techniques are involved in. This high efficiency stems from two major aspects, i.e. first, the high pressure that accelerates the densification process and second, the lower sintering temperature (Fig. 3) of the powder together with the shorter sintering time (Fig. 6) that result in a sharp decrease in the grain size of the specimens.

We believe that a quick hot pressing accompanied with two-step sintering (two-step hot press sintering) is the best sintering process to control the microstructure of ZnO ceramics. This approach is in our progress soon.

4. Conclusion

Sintering behavior of nanocrystalline ZnO powder using hot pressing method was investigated and was compared to the samples obtained by two-step sintering and conventional method. Among the conclusions are

(1) A relatively full density of 99% TD with the mean grain size of about 1.4 μm was obtained for the samples, hot pressed at 850 °C.
(2) The comparative studies showed that the sintering efficiency of HP is higher than other methods and it managed to provide the maximum density for the HP specimens.
(3) The final grain size of the hot-pressed specimens was found to be greater than that of TSS method. However, the ultra-prolonged sintering total time concerning with two-step

sintering and the lower density of the specimens restrict the practical application of this method.

References

[1] P. Duran, J. Tartaj, C. Moure, Fully dense, fine-grained, doped zinc oxide varistors with improved nonlinear properties by thermal processing optimization, J. Am. Ceram. Soc. 86 (8) (2003) 1326–1329.

[2] J. Wang, L. Gao, Photoluminescence properties of nanocrystalline ZnO ceramics prepared by pressureless sintering and spark plasma sintering, J. Am. Ceram. Soc. 88 (6) (2005) 1637–1639.

[3] M. Mazaheri, A.M. Zahedi, M.M. Hejazi, Processing of nanocrystalline 8 mol% yttria-stabilized zirconia by conventional, microwave-assisted and two-step sintering, Mater. Sci. Eng. A 492 (2008) 261–267.

[4] L. Gao, Q. Li, W. Luan, Preparation and electric properties of dense nanocrystalline zinc oxide ceramics, J. Am. Ceram. Soc. 85 (4) (2002) 1016–1018.

[5] C.M. Mo, Y.H. Li, Y.S. Liu, Y. Zhang, L.D. Zhang, Enhancement of photoluminescence in assemblies of nano ZnO particles/silica aerogels, J. Appl. Phys. 83 (8) (1998) 4389–4391.

[6] K.F. Cai, X.R. He, L.C. Zhang, Fabrication, properties and sintering of ZnO nanopowder, Mater. Lett. 62 (2008) 1223–1225.

[7] D.R. Clarke, Varistor ceramics, J. Am. Ceram. Soc. 82 (3) (1999) 485–502.

[8] A.N. Kiselve, F. Sarrazit, E.A. Stepantsov, E. Olsson, T. Claeson, V.I. Bondarenko, R.C. Pond, N.A. Kiselev, High resolution electron microscopy of ZnO grain boundaries in bicrystals obtained by the solid-phase inetergrowth process, Philos. Mag. A 76 (1997) 633–655.

[9] T.K. Roy, D. Bhowmick, D. Sanyal, A. Chakrabarati, Sintering study of nano-crystalline zinc oxide, Ceram. Int. 34 (2008) 81–87.

[10] J. Han, P.Q. Mantas, A.M.R. Senos, Densification and grain growth of Al-doped ZnO, J. Mater. Res. 16 (2) (2001) 459–468.

[11] A. Sedky, M. Abu-Abdeen, A.A. Almulhem, Nonlinear I–V characteristics in doped ZnO based-ceramic varistor, Physica B 388 (2007) 266–273.

[12] M. Mazaheri, Z. Razavi hesabi, S.K. Sadrnezhaad, Two-step sintering of titania nanoceramics assisted by anatase-to-rutile phase transformation, Scripta Materialia 59 (2008) 139–142.

[13] M. Mazaheri, M. Valefi, Z. Razavi Hesabi, S.K. Sadrnezhaad, Two-step sintering of nanocrystalline $8Y_2O_3$ stabilized ZrO_2 synthesized by glycine nitrate process, Ceram. Int. 35 (2009) 13–20.

[14] M. Mazaheri, A.M. Zahedi, S.K. Sadrnezhaad, Two-step sintering of nanocrystalline ZnO compacts: effect of temperature on densification and grain growth, J. Am. Ceram. Soc. 91 (2008) 56–63.

[15] A. Weibel, R. Bouchet, R. Denoyel, P. Knauth, Hot pressing of nanocrystalline TiO_2 (anatase) ceramics with controlled microstructure, J. Eur. Ceram. Soc. 27 (2007) 2641–2646.

[16] P. Dahl, I. Kaus, Z. Zhao, M. Johnsson, M. Nygren, K. Wiik, T. Grande, M.A. Einarsrud, Densification and properties of zirconia prepared by three different sintering techniques, Ceram. Int. 33 (2007) 1603–1610.

[17] A.P. Hynes, R.H. Doremus, R.W. Siegel, Sintering and characterization of nanophase zinc oxide, J. Am. Ceram. Soc. 85 (8) (2002) 1979–1987.