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ScienceDirect
Ceramics International 35 (2009) 1317–1320
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Influence of ball milling on the sintering behaviour of ZnO powder

Y.W. Lao, S.T. Kuo, W.H. Tuan *

Department of Materials Science and Engineering, National Taiwan University, Taipei 10764, Taiwan

Received 11 October 2007; received in revised form 29 April 2008; accepted 17 June 2008
Available online 25 July 2008

Abstract

A high purity ZnO powder was milled with either YSZ or Al_2O_3 balls. The weight losses of YSZ and Al_2O_3 balls after milling for 4 h are 10 and 40 ppm, respectively. The debris of the milling media acts as sintering aid to the ZnO powder. As a result, the grain size of the sintered ZnO specimens is reduced. The ratio of the grain boundary energy over surface energy is also decreased.

Keywords: A. Milling; B. Microstructure-final; D. ZnO

1. Introduction

Zinc oxide (ZnO) is a potential material for many applications such as varistor, displays, gas sensors [1–3], etc. For each application, additives are needed to modify the defect concentration within the ZnO grains and/or the chemistry of grain boundary. In order to mix ZnO with the additives, a milling technique is usually employed. Yttria-stabilized ZrO_2 (YSZ) and alumina (Al_2O_3) balls are the most popular milling media. However, the milling process may also contaminate the powder.

The performance of ZnO is sensitive to the presence of some additives even when their amount is very low. For example, a very small amount, 500 ppm of $Al(NO_3)_3{\cdot}9H_2O$, could increase the donor density and enhance the voltage–current nonlinearity [4]. An amount of 800 ppm of Ag can increase the grain boundary resistance of ZnO by 35-fold [5]. Therefore, the performance of ZnO-based components is sensitive to the processing environment. The effect of the milling media on the sintering behaviour of ZnO is investigated in the present study.

2. Experimental procedures

A high-purity ZnO powder (60 g), YSZ balls (535.5 g) or Al_2O_3 balls (328.2 g) with diameter of 10 mm, polyester (PE) jar with internal volume of 600 cm^3, and ethanol (300 cm^3) were used in the milling experiment. The milling media filled half of the volume of the container. A turbo mixer (T2F Turbula, Willy A Bachofen AG, Switzerland) was used for milling. The weight loss of the media after 4 h milling was recorded. The same procedure was repeated for four times. After drying the slurry, the dried lumps passed a #150 sieve to remove the agglomerates. Green compacts, 10 mm diameter and 3 mm thick, were prepared by uniaxial pressing at 50 MPa. Sintering was performed with a dilatometer or a box furnace. The heating rate was 5 °C/min. The cross-section of the specimens was ground with silicon carbide particles and polished with alumina particles. The grain boundaries were revealed by soaking the polished section in dilute hydrochloric acid. The microstructure was observed by using scanning electron microscopy (SEM). The SEM micrographs were then digitized by using a scanner. The image analysis was performed on the digitized images in order to determine the area of each grain. Over 500 grains were measured for each composition. The equivalent circular diameter was determined from the area, assuming that each grain was spherical. The mean grain size was calculated by multiplying the mean equivalent circular diameter by 1.5.

3. Results and discussion

Table 1 shows the weight loss of the milling media after 4 h milling. The average weight loss of four test runs from the YSZ and Al_2O_3 balls is 10 and 40 ppm, respectively. Milling is a process involving complex mechanical forces. The weight loss from the Al_2O_3 balls after milling is four times that from the

* Corresponding author. Tel.: +886 2 23659800; fax: +886 2 23634562.
E-mail address: tuan@ccms.ntu.edu.tw (W.H. Tuan).

0272-8842/$34.00
doi:10.1016/j.ceramint.2008.06.015

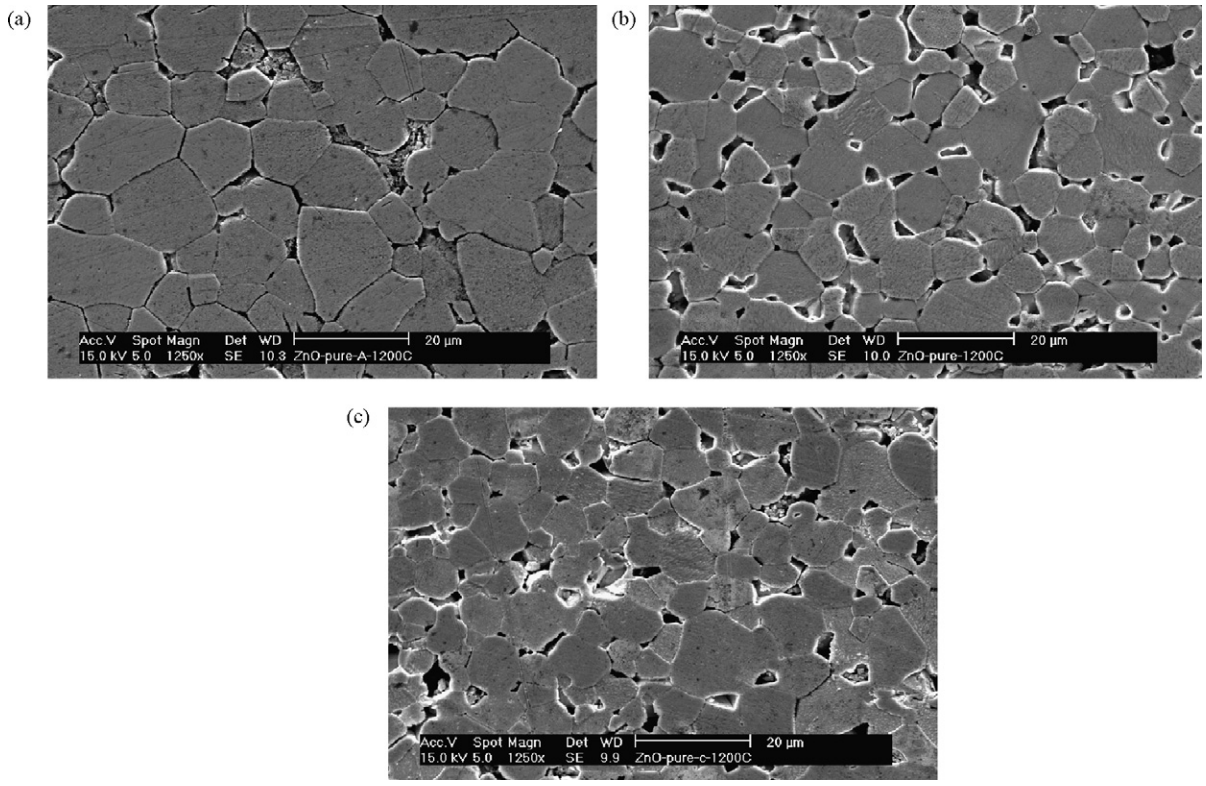

Fig. 1. Typical micrographs of the ZnO specimens prepared by using the (a) as-received powder and the powder milled by the (b) YSZ balls and (c) Al_2O_3 balls.

YSZ balls. Though the hardness of alumina is double that of the zirconia, the toughness of YSZ is double that of Al_2O_3 [6]. It suggests that the wear behaviour of the milling balls is dominated by brittle fracture. After milling, the wear debris would mix into the powder. The microstructure of the specimens is uniform after sintering, Fig. 1, implying that the mixing of the wear debris and ZnO particles is uniform. The milling process can thus be treated as a technique to mix a small amount of additive into powder.

The size of ZnO grains is the largest in the specimen prepared by using the as-received powder. The shape of pores in the specimen prepared by using the as-received powder is different from that of the pores in the ball-milled specimens. The size distribution of the ZnO grains is shown in Fig. 2. The curves follow roughly the log-normal distribution. The average grain size and size scattering in terms of standard deviation for the ZnO specimens are shown in Table 2. Though the average size of ZnO grains is different, the coefficient of variation (C.V.) for the size scattering is very close to each other.

The shrinkage rates of the powder compacts prepared by milling with YSZ and Al_2O_3 balls are shown in Fig. 3. The shrinkage rate of the compact prepared by using the as-received ZnO powder is also shown for comparison. The shrinkage of the powder compacts prepared by ball milling is slower than that of the as-received powder. Though the shrinkage rate curves are very similar to each other, there is a small hump observed in the curve for the specimens prepared by using the as-received powder. It indicates that there are two populations of pores present in the powder compacts; the small pores are at the intra-agglomerated sites and large ones at inter-agglomerated site [7]. There is no small peak observed in the specimens prepared by using the milled powders, indicating that the agglomerates are destroyed during milling. The average grain size follows the same trend as that of the density. The grain size distribution

Table 1
Weight loss of milling media after milling with ZnO powder for 4 h

Milling media (no. of test)	Weight loss (ppm)	Average weight loss (ppm)
YSZ (run 1)	11.6	
YSZ (run 2)	9.0	10.4 ± 1.1
YSZ (run 3)	10.8	
YSZ (run 4)	10.1	
Al_2O_3 (run 1)	32.9	
Al_2O_3 (run 2)	51.5	38.4 ± 8.9
Al_2O_3 (run 3)	32.6	
Al_2O_3 (run 4)	36.6	

Table 2
Microstructure characteristics of ZnO specimens after sintering at 1200 °C for 1 h

	Average grain size (μm)	Standard deviation (μm)	C.V.* (%)
As-received	14.5	5.8	40
YSZ milling media	11.0	4.6	41
Al_2O_3 milling media	9.9	3.9	39

**Note*: C.V. = coefficient of variation = (standard deviation)/(average grain size).

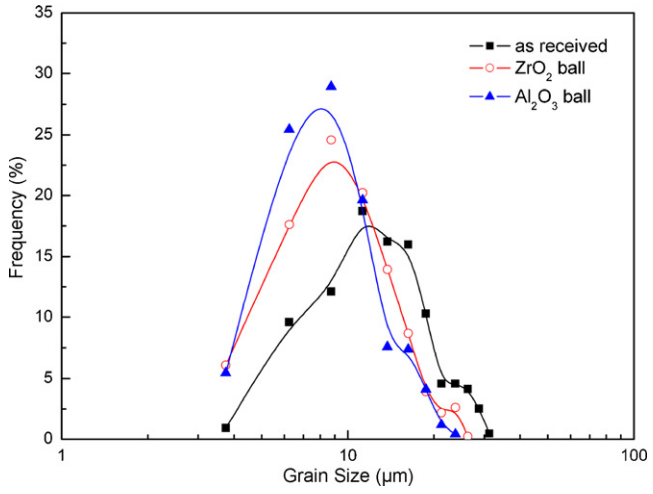

Fig. 2. Size distribution of ZnO grains in the ZnO specimens after sintering at 1200 °C for 1 h.

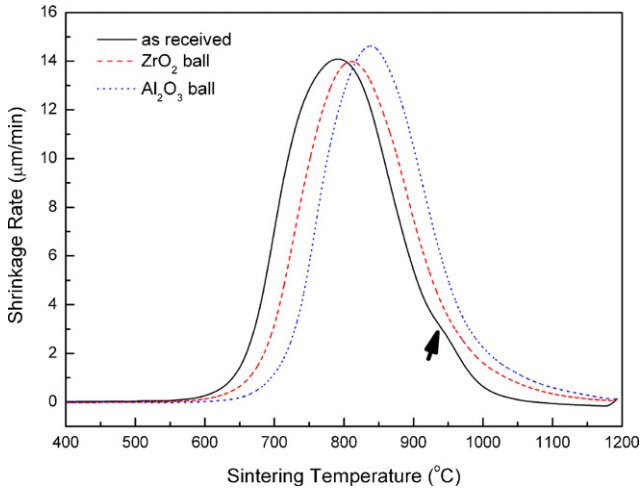

Fig. 3. Densification rate of the ZnO specimens as a function of temperature.

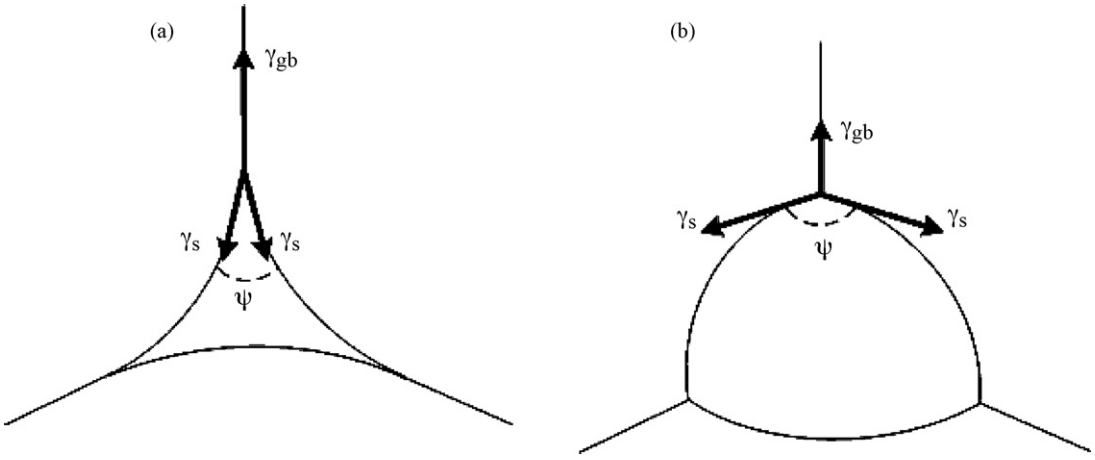

Fig. 4. Balance between surface energy (γ_s) and grain boundary energy (γ_{gb}) for (a) pure ZnO and (b) ZrO_2 and Al_2O_3-doped ZnO specimens.

curves of the three specimens are very similar; furthermore, the pores are mainly located at the triple junctions and no pores trapped within the ZnO grains (Fig. 1). It indicates that the pores move with the grain boundaries during sintering. The growth of ZnO grains thus follows the trend of density increase.

It is worth noting that the pore shape is changed due to the addition of the ZrO_2 and Al_2O_3 dopants. The dihedral angle of pure ZnO is usually small [8]. Many additives, such as Bi_2O_3, may increase the value of the dihedral angle. The value of the dihedral angle (ψ) is the balance between grain boundary energy (γ_{gb}) and surface energy (γ_s) as

$$\cos\frac{\psi}{2} = \frac{1}{2}\frac{\gamma_{gb}}{\gamma_s} \quad (1)$$

The presence of ZrO_2 and Al_2O_3 dopants may modify both grain boundary energy and surface energy to different extent. Since the dihedral angle is increased, this indicates that both the ZrO_2 and Al_2O_3 additives reduce the ratio grain boundary energy/surface energy, as suggested in Fig. 4.

4. Conclusions

The densification and grain growth rates of ZnO are slowed down after milling with zirconia and alumina balls. The presence of zirconia and alumina milling debris can also reduce the dihedral angle; the densification and grain growth behaviour of ZnO are therefore affected.

References

[1] W.G. Carlson, T.K. Gupta, Improved varistor nonlinearity via donor impurity doping, J. Appl. Phys. 53 (8) (1982) 5746–5753.
[2] R. Ghosh, G.K. Paul, D. Basak, Effect of thermal annealing treatment on structural, electrical and optical properties of transparent sol–gel ZnO thin films, Mater. Res. Bull. 40 (11) (2005) 1905–1914.
[3] P. Nunes, E. Fortunato, P. Vilarinho, R. Martins, Effect of different dopants on the properties of ZnO thin films, Int. J. Inorg. Mater. 3 (2001) 1211–1213.
[4] J. Fan, R. Freer, The roles played by Ag and Al dopants in controlling the electrical properties of ZnO varistors, J. Appl. Phys. 77 (9) (1995) 4795–4800.

[5] S.T. Kuo, W.H. Tuan, J. Shieh, S.F. Wang, Effect of Ag on the microstructure and electrical properties of ZnO, J. Eur. Ceram. Soc. 27 (16) (2007) 4521–4527.
[6] R. Morrell, Handbook of properties of technical & engineering ceramics: Part 1, in: An Introduction for the Engineer and Designer, National Physical Lab, London HMSO, 1985.
[7] A. Roosen, H. Hausner, Sintering kinetics of ZrO_2 powders, Adv. Ceram. 12 (1984) 714–726.
[8] J.-H. Choi, N.-M. Hwang, D.-Y. Kim, Pore–boundary separation behavior during sintering of pure and Bi_2O_3-doped Zno ceramics, J. Am. Ceram. Soc. 84 (6) (2001) 1398–1400.