

Fabrication of Dense ZnO-Varistors by Atmosphere Sintering

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Abstract

ZnO varistors are fabricated by the atmosphere sintering, during which Bi₂O₃ vapor is transferred from the atmosphere powder bed to the pure ZnO powder compacts. The residual porosity of the atmosphere sintered specimens is significantly lower than that of the conventionally liquid-phase sintered specimens. The densification process during the atmosphere sintering is discussed and the electrical characteristic of the atmosphere sintered varistors is examined. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

When the ZnO varistors are used for surge absorbing, voltage is continuously applied to the varistors and a small amount of current always leaks.^{1,2} Such leakage current and consequent temperature rise of the varistor may cause an ultimate thermal runaway of the device.^{1,3,4} Therefore, the ZnO varistors should be designed to prevent the eventual temperature rise. A high value of surface area/volume ratio and the high thermal conductivity are required for rapid heat dissipation. In addition, the large heat capacity of the ZnO varistor is desirable for enhancing its energy handling capabilities.^{1–3}

In this respect, the homogeneous and pore-free microstructure of the ZnO varistor is essential to increase its reliability and lifetime. Since the current always flows through the easiest path

between the electrodes, the nonuniformities in the microstructure, for instance, the presence of pores and nonuniform size distribution of ZnO grains, will make the varistor more susceptible to hot spots.^{1–5} The pores are particularly detrimental because they not only decrease the thermal conductivity but also lower the heat capacity of the varistor.

The aim of this work was, therefore, to fabricate the pore-free ZnO varistors. Instead of the conventional sintering of ZnO powder previously mixed with Bi₂O₃ and other oxides, the atmosphere sintering⁶ has been adopted in this study. The powder compacts of pure ZnO and 99ZnO–1MnO₂ (in mole%) were sintered in Bi₂O₃ atmosphere by placing Bi₂O₃ powders in a closed alumina crucible. During the conventional sintering of ZnO–Bi₂O₃, relatively large pores were observed to form during the very beginning stage of sintering. Such pore formation did not occur during atmosphere sintering and thus an almost pore-free microstructure could be obtained.

2 Experimental Procedure

The starting materials were reagent-grade ZnO[†], Bi₂O₃[‡] and MnO₂[§]. The average particle sizes of ZnO and Bi₂O₃ powder determined by sedimentation technique[¶] were 0.5 and 10 μm, respectively. The Bi₂O₃ powder was milled with attritor for 1 h and its average particle size after milling was determined to be 3 μm. In the MnO₂ powder, the particles of very large size were present. The powders were therefore suspended in ethanol and settled in a column for 10 min, and then the settled particles were discarded. From the Stokes' relation,⁷ the largest particle in MnO₂ used in this experiment was predicted to be 7 μm.

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[†]ZnO: 99.9%, Aldrich Chem. Co. Inc., Milwaukee, WI, USA.

[‡]Bi₂O₃: 99.9%, Aldrich Chem. Co. Inc., Milwaukee, WI, USA.

[§]MnO₂: 99.9%, Shimakyu Yakuhin & Co., Ltd., Osaka, Japan.

[¶]SediGraph 5100-A v2.03, Micromeritics Instrument Co., Norcross, GA., USA.

Powder compacts of pure ZnO, 99ZnO–1MnO₂ and 98ZnO–2Bi₂O₃ (in mole%) were prepared. The powder mixtures of 99ZnO–1MnO₂ and 98ZnO–2Bi₂O₃ were wet-milled for 1 h with ethanol. After drying, the powders were compacted into cylindrical specimens of 5 mm in diameter and approximately 5 mm in height and pressed again hydrostatically at 150 MPa. The green densities of the powder compacts were approximately 58% of theoretical. The obtained compacts were placed on a platinum foil in a closed alumina crucible and sintered at 1200°C for 1 h.

During sintering of pure ZnO and 99ZnO–1MnO₂, the powder mixture of ZnO and Bi₂O₃ was placed as an atmosphere powder bed. The compacts, however, were not in direct contact with the atmosphere powder bed. Preliminary experiments with the powder mixture of varying ZnO to Bi₂O₃ mole ratio showed that the resultant electrical characteristics of the specimen were optimum when its ratio was 1:1. This composition was hence chosen for the powder bed. On the other hand, the compacts of 98ZnO–2Bi₂O₃ were sintered normally without atmosphere powders. The heating and the cooling rates were 5 and 10°C min⁻¹, respectively. In order to observe the difference in densification behavior during normal and atmosphere sintering, the compacts were also sintered at temperatures ranging from 600 to 1000°C. Compacts were heated to a desired temperature and sintered for 1 h, and porosities were determined by using the water-immersion method or point counting method. In addition, DTA experiment was carried out for the 98ZnO–2Bi₂O₃ specimens to detect the liquid-forming temperature.

For microstructural observation, the sintered specimens were polished and etched with 50% HF solution for 25 s. The I–V characteristics of the atmosphere sintered 99ZnO–1MnO₂ specimens were measured with a picoammeter.* The specimen was sliced and ground to 0.5 mm in thickness and the electrode was made by sputtering Au on each surface.

3 Results and Discussion

Figure 1(a) and (b) show the microstructures of pure ZnO and 99ZnO–1MnO₂ specimen, respectively, sintered for 1 h at 1200°C in atmosphere. The microstructure of a conventionally liquid-phase sintered 98ZnO–2Bi₂O₃ specimen sintered in same conditions is shown in Fig. 1(c). For comparison, that of a commercial ZnO varistor (Model: Δ ZNR

10k 821 75, Matsushita Electrical Industrial Co., Osaka, Japan) is also presented in Fig. 1(d). As can be observed, the specimens sintered in Bi₂O₃ atmosphere [Fig. 1(a) and (b)] showed much lower porosity than the conventionally sintered ones [Fig. 1(c) and (d)]. The porosities measured by the point counting method for the atmosphere sintered specimens were less than 0.5%, whereas the porosities of the specimens shown in Fig. 1(c) and (d) were 8 and 4.2%, respectively.

During the atmosphere sintering, a slight amount of Bi₂O₃ is predicted to transfer from the atmosphere powder bed to the specimen due to its high vapor pressure. The equilibrium partial pressures of Bi and O₂ at 831°C have been reported to be 1.18×10^{-1} and 0.61×10^{-1} Pa, respectively.⁸ The weight gain of the specimen after the atmosphere sintering at 1200°C was determined to be around 3.7%. The overall compositions of the specimen shown in Fig. 1(a) and (b) are thus predicted to be 99.4ZnO–0.6Bi₂O₃ and 98.4ZnO–1MnO₂–0.6Bi₂O₃ (in mole%), respectively. The liquid phase mainly present at the triple grain boundary junctions was observed to be distributed uniformly throughout both the atmosphere and conventionally sintered specimens. Note also that the commercial varistor specimen [Fig. 1(d)] showed a lot of second phase particles probably due to the other additive oxides.

Figure 2 shows the change in porosity of the specimens as a function of sintering temperature. After sintering at 600°C for 1 h, the porosity of the 98ZnO–2Bi₂O₃ specimen was 38% while that of atmosphere sintered pure ZnO specimen was 23%.

Compared to the green density of the powder compacts, it can be deduced that a significant densification has already occurred during atmosphere sintering of pure ZnO even at this low temperature and that the presence of Bi₂O₃ in powder compact has greatly retarded this initial densification. The retardation of initial densification in ZnO powder compact by the addition of Bi₂O₃ was also reported by Kim *et al.*⁹ During constant-rate heating, for instance, 10% of linear shrinkage was reached at 800°C for pure ZnO specimen but the 0.1% addition of Bi₂O₃ shifted it to about 900°C. Furthermore, the densification process of pure ZnO has been reported to be significant at low temperatures such as 600°C and be almost completed for about 1 h at 900°C.

In the 98ZnO–2Bi₂O₃ specimen, however, a rapid densification was observed to occur during sintering at 700°C. The porosity decreased to 6%, and the specimens sintered at and above 700°C showed practically no open pores. The porosity of the pure ZnO specimen sintered in atmosphere at 700°C was also around 6%. With further increase

*Model: 4140B pA Meter/DC voltage source, Yokogawa Hewlett Packard Co., Yokogawa, Japan.

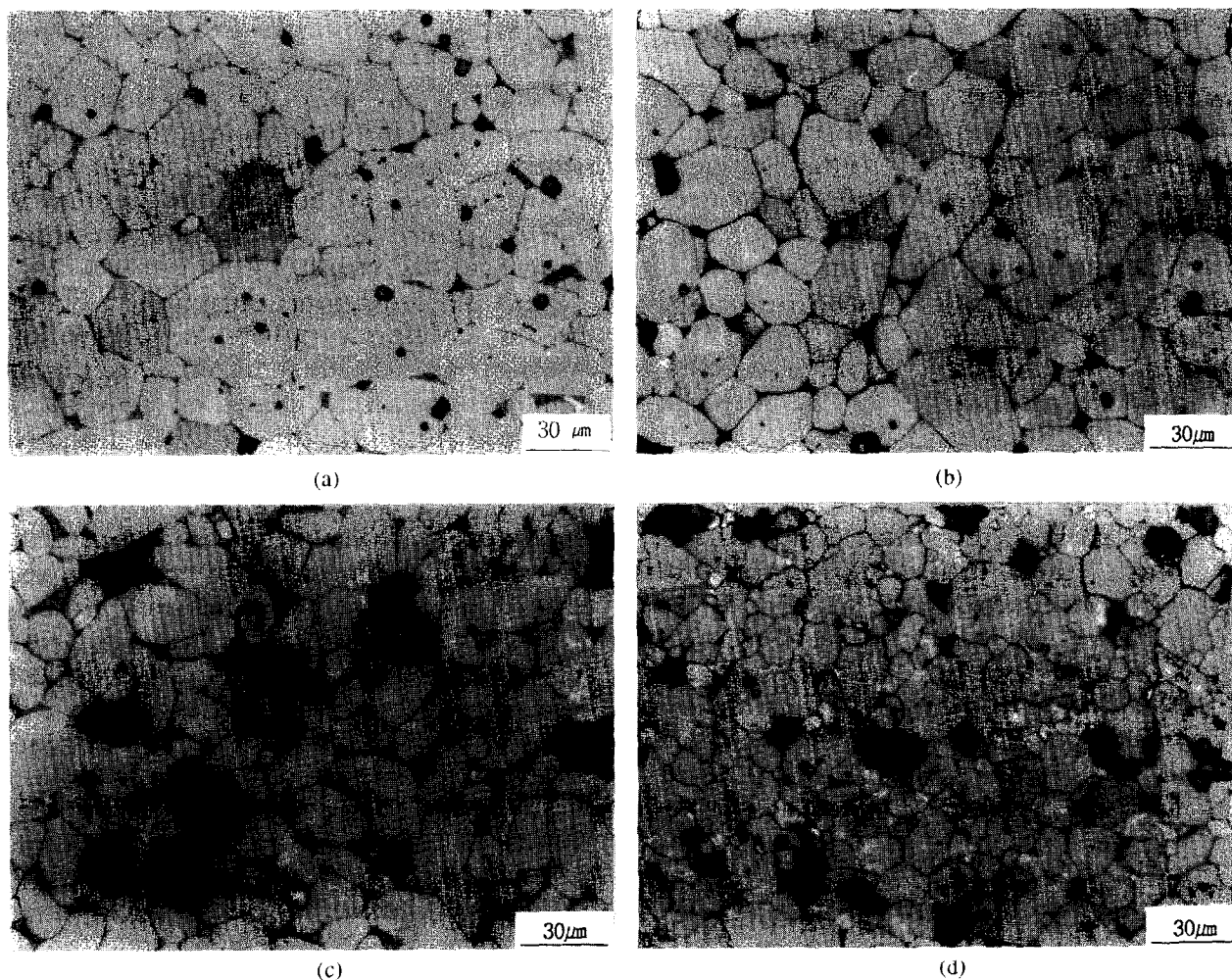


Fig. 1. Microstructures of the atmosphere-sintered (a) pure ZnO, (b) 99ZnO-1MnO₂, (c) the conventionally sintered 98ZnO-2Bi₂O₃ specimen treated at 1200°C for 1 h, and (d) the commercial varistor.

of sintering temperature up to 1200°C, it was found that the porosity of atmosphere sintered ZnO specimen decreased continually to 0.5%. On the other hand, that of the liquid-phase sintered 98ZnO-2Bi₂O₃ specimen also decreased to 5%

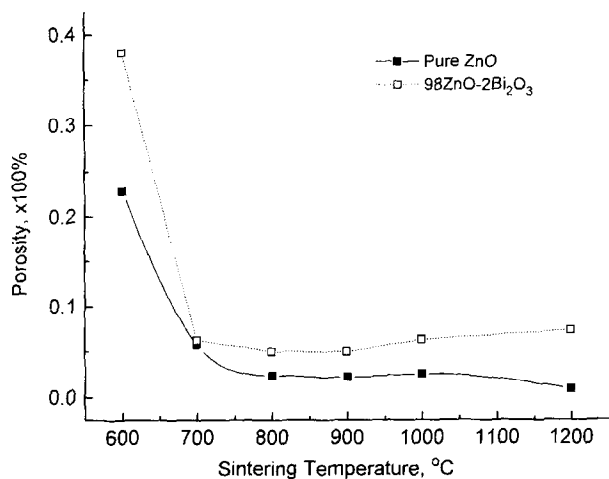


Fig. 2. Variations in porosity during the atmosphere and normal sintering; the pure ZnO and 98ZnO-2Bi₂O₃ specimens were used, respectively.

after sintering at 900°C but increased again steadily to 8% with the increase of sintering temperature to 1200°C.

Figure 3 shows the result of DTA for the 98ZnO-2Bi₂O₃ powder compact, which reveals the formation of a liquid at 745°C. This result is in accordance with that reported earlier.¹⁰ In this respect, the substantial densification observed in the 98ZnO-2Bi₂O₃ specimen at 700°C is not predicted

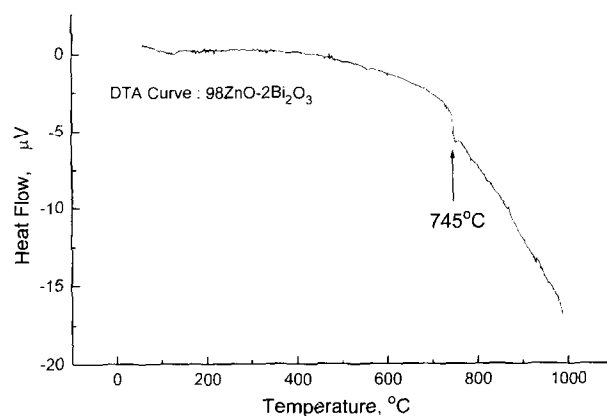


Fig. 3. DTA curve for the 98ZnO-2Bi₂O₃ powder mixture.

to be the consequence of liquid-phase sintering. The observation that the density increases significantly before the appearance of liquid has also been made in W-Ni-Fe alloy.¹¹ Most of its densification had occurred in solid state during heating at temperatures (between 1200 and 1250°C) much below the liquid-phase sintering temperature. However, the mechanism of pronounced densification before the appearance of liquid is not well understood at present.

Figure 4 shows the microstructures of the specimens after sintering at 700°C for 1 h. Although both the 98ZnO-2Bi₂O₃ and pure ZnO specimens exhibited the same porosity after sintering at this temperature (Fig. 2), their microstructures are quite different. The microstructure of the 98ZnO-2Bi₂O₃ specimen shown in Fig. 4(a) is composed of the apparently dense regions and large pores. The size of pores was observed to range from 2 to 20 μm. On the contrary, the pure ZnO specimen [Fig. 4(b)] sintered in the Bi₂O₃ atmosphere exhibited much smaller pores with the largest size of around 5 μm. The formation of large pores in the 98ZnO-2Bi₂O₃ specimen is believed to be the

consequence of substantial and rapid increase in density at this temperature. Note, during such substantial shrinkage, that even a slight variation in rate of local densification may result in the formation of large pores. On the other hand, the pores of large size may not be formed in the atmosphere sintered specimen because the densification occurs slowly and continuously.

When the liquid-phase sintering temperature is reached, for instance at 800°C, the densities of the specimens were already so high that the rearrangement of solid particles exerted by the liquid capillary pressure observed in usual liquid-phase sintering is not expected to occur. Instead, only a small amount of isolated pores remain at this temperature, which are known^{11,12} to be eventually eliminated by the liquid flow from the surrounding dense regions to the pores; the small pores were observed to be filled before the large ones. It is thus apparent that the formation of large pores in the beginning stage of sintering is detrimental to achieving a full densification.

The porosity increase of the 98ZnO-2Bi₂O₃ specimen in Fig. 2 confirms the previous results⁹ showing that increasing the sintering temperature higher than 900°C results in increased porosity. The porosity increase was presumed to result from either impurity or ZnO evaporation. From the porosity which decreased continuously with temperature during atmosphere sintering, however, the pore formation due to evaporation is not believed to be the main cause of porosity increase in ZnO-Bi₂O₃ system. It is more likely to arise from pore coalescence as a consequence of grain growth and pore coarsening due to the difference in curvature between small and large pores. An analysis¹² of the balance between the pore pressure and the liquid capillary pressure during liquid-phase sintering has shown that pore growth is the major cause of porosity increase. In this respect, the initial size of isolated pores is expected to critically influence the sintering of the ZnO-Bi₂O₃ ceramics. When they are small, they are eliminated by the subsequent pore filling by liquid as observed in the atmosphere sintered specimens. When they are large and thus stable, on the other hand, the pores grow so that the porosity increases with sintering temperature.

Figure 5 shows the current-voltage characteristics of the atmosphere sintered 99ZnO-1MnO₂ specimen and the commercial varistor shown in Fig. 1(d). As can be observed, the specimen exhibited a nonlinear current-voltage characteristic and the nonlinear exponent coefficient α was determined to be 25. On the other hand, the α for the commercial varistor specimen was 35 and its leakage current at the prebreakdown region was 2 orders of magnitude smaller than that of the specimens

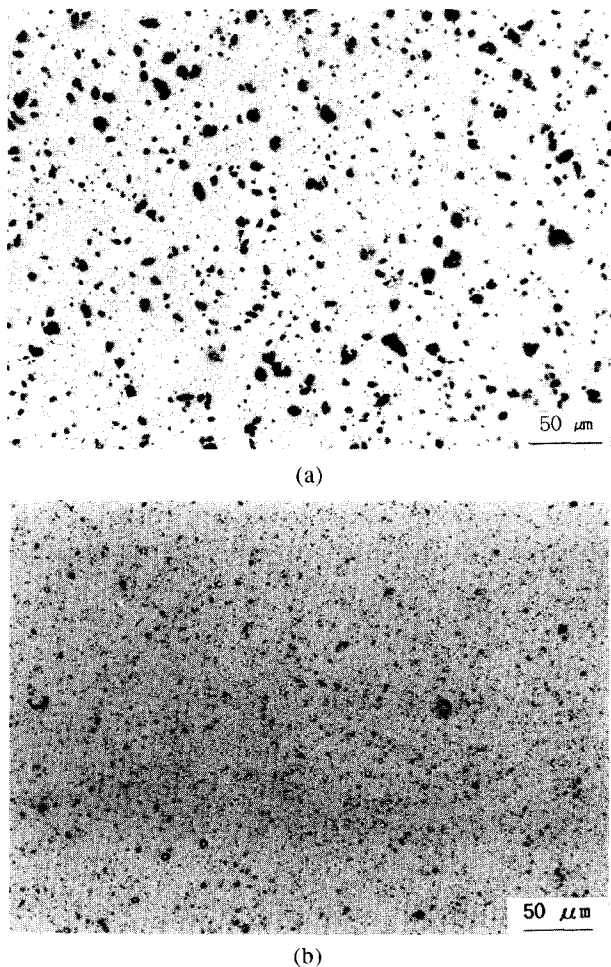


Fig. 4. Microstructures of (a) the atmosphere sintered pure ZnO and (b) the 98ZnO-2Bi₂O₃ specimen treated at 700°C for 1 h.

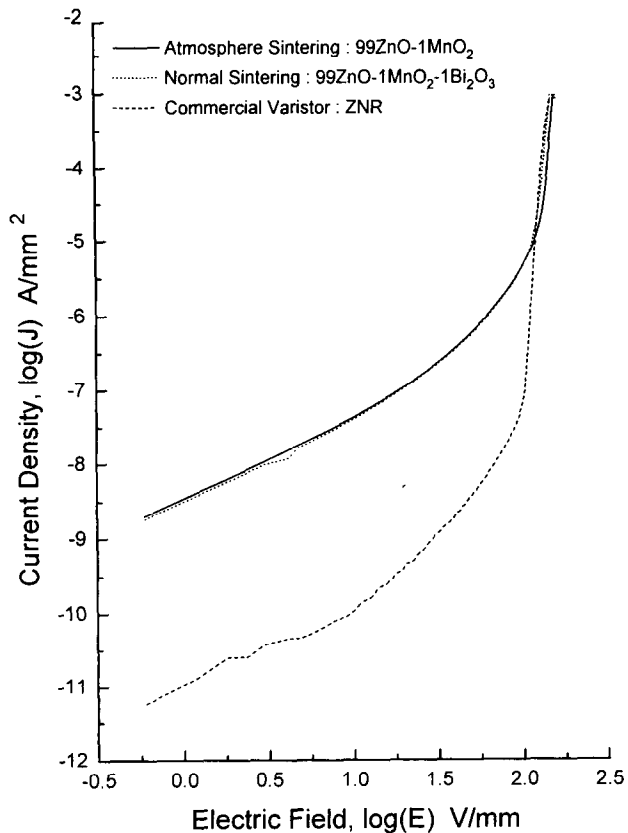


Fig. 5. Current-voltage characteristics of the atmosphere sintered 99ZnO-1MnO₂ and the conventionally sintered 98ZnO-1MnO₂-1Bi₂O₃ specimen sintered at 1200°C for 1 h. Dashed line is for the commercial varistor shown in Fig. 1(d).

prepared in this experiment. These differences can be explained in terms of various additive oxides such as CoO, Sb₂O₃ and Cr₂O₃ which are known to increase the α and to decrease the leakage current.^{1,2,13} Furthermore, Gambino and others¹⁴⁻¹⁷ have observed the increase of leakage current with the amount of Bi₂O₃. Compared to the commercial varistor specimen [Fig. 1(d)], a larger amount of liquid was observed in the specimen shown in Fig. 1(b).

4 Conclusions

By sintering the ZnO powder compact in Bi₂O₃ atmosphere, the varistor specimens with a very small amount of porosity could be obtained. During conventional sintering of the ZnO-Bi₂O₃ powder compact, the densification at very low temperature, for instance at 600°C, was observed to be negligible compare to that of pure ZnO. On the other hand, a rather rapid and pronounced densification occurred at 700°C, which might lead to the formation of isolated pores of very large size. During the subsequent liquid-phase sintering of a specimen containing large and stable pores, the pore coarsening occurred and the porosity

increased. The results also showed that, during the conventional liquid-phase sintering of ZnO varistor, a significant shrinkage occurs during heating before the appearance of any liquid.

When the pure ZnO powder compact was sintered in Bi₂O₃ atmosphere, the densification began at much lower temperatures than ZnO-Bi₂O₃ mixtures and the densification proceeded slowly and continuously during heating. Therefore, the formation of such large isolated pores due to rapid densification was suppressed. The small size isolated pores were eliminated during subsequent liquid-phase sintering.

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