

Fabrication of ZnO electroceramics by reaction bonding

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ZnO ceramics doped with small amounts of Bi₂O₃, CoO, MnO, Sb₂O₃ and Cr₂O₃ offer a great potential as electroceramic materials to be used as protectors to prevent electric surges. In the present communication, the reaction bonded alumina oxide (RBAO) technique is adapted for the production of ZnO-based ceramics by the reaction bonding zinc oxide (RBZnO) process with the idea of achieving the advantages of the RBAO process. Because Zn oxidation occurs between 330 °C and 468 °C, slow heating rates before the Zn melting point (419 °C) is very important in order to obtain the desired ceramic. The need for a fine microstructure of the matrix with many grain boundaries is discussed.

Key words: Milling, Powders-solid state reaction, Sintering, ZnO, Varistors.

Introduction

A ZnO-based varistor is a ceramic device used as a protector to prevent electric surges. The behavior of the current-voltage (I-V) curve in varistors is non-linear and can be explained by the presence of Schottky barriers at the grain boundaries [1-3]. Varistors can work with either alternatives or direct current over a wide range of power or voltage values. Additionally, varistors have a high capacity to absorb energy, presenting good stability with time. The versatility of varistors enables their use in high voltage applications as well as in microelectronic circuitry.

Fabrication of ZnO-based varistors consists in mixing ZnO powders (> 95 wt.%) with other oxide powders such as Bi₂O₃, CoO, MnO, Sb₂O₃ and Cr₂O₃, followed by consolidation and conventional sintering [4]. From this process a polycrystalline microstructure results consisting of semiconducting fine grains of ZnO surrounded by an isolating Bi-rich phase. This kind of microstructure produces the desired non-linear I-V curve [5].

Reaction bonding of aluminum oxide (RBAO) is a technique developed during the last decade to produce low-shrinkage Al₂O₃-based ceramics with superior mechanical properties. In this process, metal-ceramic powder compacts containing reactive fine-grained alumina particles are oxidized and are subsequently sintered in an oxidizing atmosphere. The reaction mechanisms and the processing route for monolithic Al₂O₃ ceramics have

already been described [6-9]. The authors of this process have documented that the alumina from the RBAO process displays better physical and mechanical characteristics than the alumina obtained by a conventional process. At the same time the new alumina pieces present a homogeneous microstructure consisting of very small grains. This has motivated the goal of this study where we explore the possibility of producing ZnO by the reaction bonding zinc oxide (RBZnO) process, in order to obtain a ZnO ceramic with a fine microstructure containing many grain boundaries.

Experimental Procedure

Starting materials were a dry mixture of metallic powders of Zn, Co, Mn, Cr and Sb combined with ZnO and Bi₂O₃ powders (Final composition after reaction bonding is; 97 wt.% ZnO, 1 wt.% Sb₂O₃, 0.5 wt.% Bi₂O₃, 0.5 wt.% MnO, 0.5 wt.% Cr₂O₃ and 0.5 wt.% CoO). The powder mixture was prepared in a ball mill with a ZrO₂ media, the speed of rotation of the mill was 200 rpm for 16 h. The ball-to-powder volume ratio was 10:1. With the milled powder mixture, cylindrical samples 2 cm diameter and 0.2 cm thickness were fabricated by uniaxial pressing using 270 MPa pressure. Then the pressed samples were sintered in air following a cycle of heating that allows the Zn oxidation to produce more ZnO. A scheme of the heating cycle is presented in Fig. 1. The reason to aggregate ZnO powder in the starting mixture, and not to use pure metallic Zn, is because the original ZnO particles work as seeds or nuclei in order to obtain a complete oxidation of pure Zn, through a mechanism known as reaction bonding [8].

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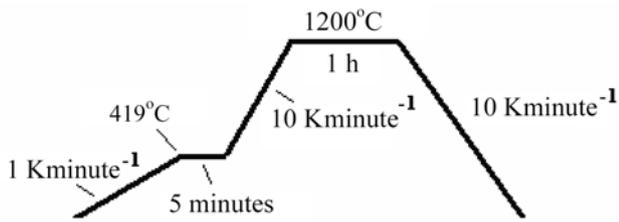


Fig. 1. Scheme of the heating cycle for the RBZnO process.

Results and Discussion

Differential thermal analysis (DTA) indicates that Zn oxidation occurs between temperatures of 330 °C and 468 °C. The melting point of Zn is at 419 °C, thus the heating during sintering has to be very slow below 419 °C for complete solid Zn oxidation during heating in accordance with Claussen [9], who has reported that metal oxidation in the RBAO process is better below the melting point of the metal, in order to obtain fine microstructures in the ceramic produced.

X-ray diffraction analysis (XRD) shows that all the Zn oxidized during heating when the sample was heated at rates of 1 Kminute⁻¹ between room temperature

and 419 °C. Good densifications were reached when the ceramics were sintered at 1200 °C for 1h, because the bulk density of the ZnO ceramic was $\approx 92\%$ of the theoretical density, which was calculated using the theoretical densities of the individual phases and the results of the measurements determined by the Archimedes method.

Figure 2(a-b) are scanning electron microscopy (SEM) micrographs depicting the microstructure of the fabricated material after the reaction bonding cycle. Observations show a homogeneous microstructure formed by small ZnO grains with angular shapes that are typical of these types of ceramic. The material is very porous. In Fig. 2b we see that there is some coarsening of the ZnO grains and also that some very fine prismatic crystals have formed, the later are indicated by arrows in the picture and they correspond to the new ZnO grains, their presence is a result of the RBZnO process. These new ZnO grains are localized principally at intragranular zones, however, some also are observed ZnO grains at intergranular positions. The presence of dopants could not be observed here either by X-ray diffraction or by SEM because of their very small amounts in the ZnO-based ceramic.

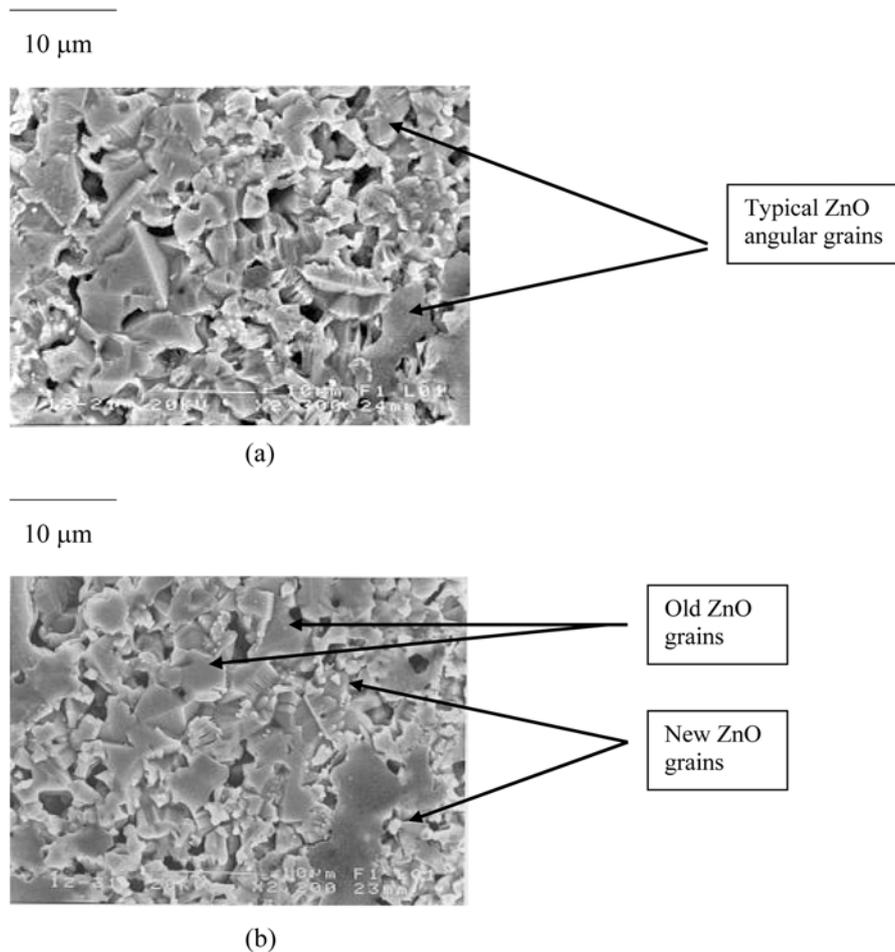


Fig. 2. Microstructure of the ZnO varistors obtained by the reaction bonded zinc oxide process. Sintered at 1200 °C for 1 h.

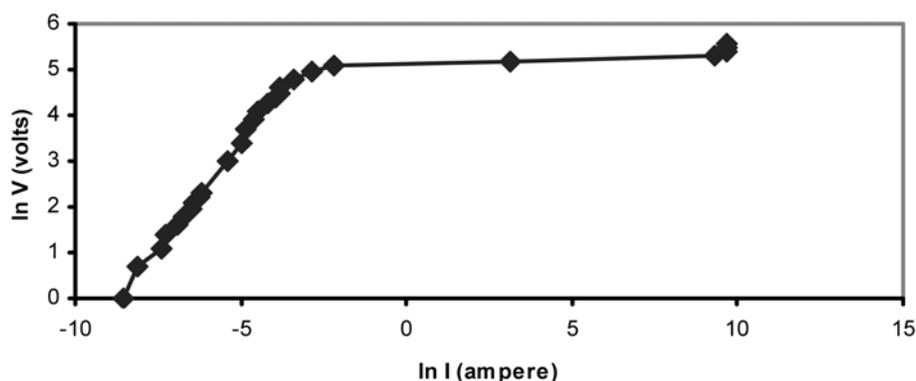


Fig. 3. Applied electric field versus current density for ZnO varistors. Sintered at 1200 °C for 1h.

Figure 3 shows a plot of applied electric field versus current density. It was observed from Fig. 3 that the threshold voltage of the ZnO-based varistors is very high. The significant very small new ZnO grain size localized in both inter and intragranular zones are the origin for this increase in the threshold voltage and decrease of the dielectric constant. As has been commented before the presence of very fine ZnO grains is attributed to the RBZnO process that encourages the formation of new ZnO at grain boundaries which hinders the old ZnO grains from growing into large particles. The performance of the electrical resistance of the ZnO electroceramics fabricated here is directly dependent on the microstructure, because with fine and homogeneous microstructures the behavior of the (I-V) curve is good, needing very large voltages in order to reach the breakdown of the sample.

Conclusions

- A new, simple and successful route to produce ZnO based electroceramics starting from cheap materials has been explored.
- It proved possible to use reaction bonding to produce ZnO-based varistor formulations starting from pure metals.

- Oxidation of Zn occurs between 330 and 468 °C, so slow heating below Zn melting point (419 °C) is very important in order to obtain the desired ceramic.
- The improved compaction behavior of RBZnO powders in comparison to the usual ZnO powders leads to a fine microstructure of the matrix with many grain boundaries.

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