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The effect of Al_2O_3 on physical & electrical properties of ZnO varistors

N. Riahi-Noori[a], R. Sarraf-Mamoory[b,]*, A. Mehdikhani[c] and A. M. Hadian[d]
[a]*Ph.D. Student, Tarbiat Modares University & Researcher, Niroo Research Institute, Tehran, Iran*
[b] *Corresponding Author and Associate Prof., Tarbiat Modares University, Tehran, Iran*
[c]*Researcher, Niroo Research Institute, Ceramic & Polymer Group, Tehran, Iran*
[d]*Associate Prof., Tehran University, Tehran, Iran*

In this paper, the effect of Al_2O_3 on physical and electrical properties of ZnO varistors was investigated. After adding different amounts of Al_2O_3 to ZnO varistors, green and fired density and 3-point bending strength were measured. Also, microstructural analysis was evaluated by SEM. Finally, the optimum values for nonlinear coefficient (α) and breakdown voltage were obtained as 50 and 638 v/cm respectively.

Key words: varistor, aluminum oxide, physical properties, electrical properties, nonlinear coefficient, breakdown voltage.

Introduction

ZnO varistors, known as semiconductor ceramic devices, have a good nonlinearity behavior in their currentvoltage curves. Manufacturing process of this product is as: mixing, forming, and sintering of ZnO powder doped with a small amounts of other oxides such as Bi_2O_3, Sb_2O_3, CaO, MnO_2, Cr_2O_3, and etc [1, 2]. These additive oxides can affect the varistor properties in two ways: a) directly, in an electrical sense, as is the case for Bi_2O_3, which segregates at the ZnO grain boundaries and relates to nonlinearity of the current-voltage characteristics or b) indirectly, by affecting the micro-structural development of the ceramic body during firing. Since the breakdown voltage is both proportional to the number of ZnO grains, which is series between the electrodes, and the average grain size of the ZnO, it is important to understand the effect of the individual metal oxide additives on the ZnO microstructural development [2].

The I-V characteristics of ZnO varistors are expressed by three distinct regions as pre-switch region, switching of breakdown region, and high-current region [2,3]. During normal operation the varistor operates as an insulator and only a small leakage current flows through the varistor (pre-switch region). When the voltage on the device reaches this level, the resistance of the varistors drops rapidly and a larger current starts running through the varistor (switching of breakdown region)[2, 4]. For a very large current the conductance of the varistor will be limited by the internal conductance of the ZnO grains, which forces the varistor into a linear electrical behavior (high current region). This is known as the upturn in the electrical characteristics [2].

Komatsu et al. [5] were the first researchers to study the effect of Al_2O_3 additives in ZnO for sintering modification. These researchers reported that an addition of 0.6 mol% Al_2O_3 to ZnO, significantly reduced the sintering rate of ZnO at temperatures between 800 and 1000 °C. Silvia Irene Nunes [6] reported on the grain growth of ZnO in ZnO-Bi_2O_3 ceramics with Al_2O_3 additions and Houabes et al. [7] worked on the effect of aluminum oxide on the residual voltage of ZnO varistors. Mao-Hua Wang et al.[8] studied the electrical charac- teristics and stability of low voltage ZnO varistors doped with Al_2O_3. However, they did not study the effect of aluminum oxide on physical and electrical properties of varistors. In this paper, the physical and electrical properties of varistors were studied when the amount of aluminum oxide was varied.

Experimental Procedure

The pure starting materials were supplied by Merck Co. Table 1 shows the common compositions of the varistor specimens and Table 2 shows the amount of Al_2O_3-doping used in prepared samples.

The powder mixtures were wet ball-milled in a polyethylene jar with ZrO_2 balls for 18 hrs in deionized water. After being dried and granulated, the powder was pressed into disc shapes of ϕ 10 $\times$ 2 mm at a pressure of 70 MPa. The discs were sintered at 1200 °C for 2 hrs followed by silver paste applied to the two faces of the discs to provide electrodes for electrical properties measurements.

The green and fired density (ρ_1 & ρ_2) of the varistor ceramics were measured by dimensional and Archimedean methods respectively. Also, the strength of all samples was measured by 3-point bending test. The microstructure was examined using a scanning electron microscope

*Corresponding author:
Tel : +9821 88011001 (ext: 3970 Lab , 3308 Office)
Fax: +9821 88005040
E-mail: rsarrafm@modares.ac.ir

Table 1. common composition of commercial varistors

NiO	MnO_2	Cr_2O_3	CoO	Sb_2O_3	Bi_2O_3	ZnO	Oxide
0.5	0.5	0.5	0.5	0.5	1	96.5	Mole %

Table 2. Variable amounts of Al_2O_3-doped in prepared samples

Code	Al_2O_3 Content (ppm)
A	0
B	50
C	100
D	150
E	200
F	250
G	300

(SEM). The nonlinear coefficient (α) was determined from $\alpha = \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1}$, where $I_1 = 0.1$ mA/cm^2, $I_2 = 1.0$ mA/cm^2, and where V_1 and V_2 are the electrical voltages corresponding to I_1 and I_2 respectively, and fracture voltages were calculated as electrical properties.

Results and discussion

The green densities of all samples with different amounts of Al_2O_3 were obtained as 2.65 ± 0.1 gcm^{-3}. Table 3 and Figure 1 show the result of fired density of specimens. The densities of fired ceramics were first gradually increased from 5.2 to 5.45 gcm^{-3} and then decreased to 5.30 gcm^{-3}.

The reason is due to the fact that the presence of 200 ppm aluminum oxide can change the viscosity of the liquid phase i.e. Bi_2O_3. As is known, a small amount of aluminum oxide can increase liquid phase viscosity and so the wetting ability of ZnO grains is increased. Then, by adding more aluminum oxide, the liquid phase will be more viscose and acts as a solid phase role, which affects sintering behavior. These are the reasons why density will be decreased again. On the other hand, very high viscosity and less liquid phase resulted in less shrinkage and a lower density.

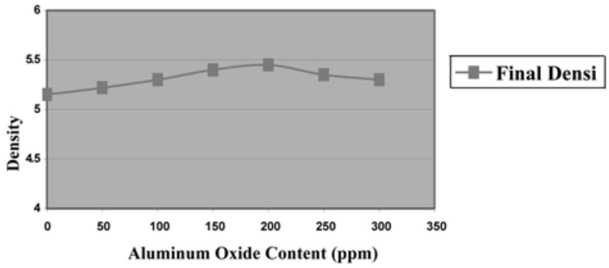

Fig. 1. The effect of aluminum oxide content on green and fired density of varistors.

Then 3-point bending strength tests for all varistor samples were carried out. The results of these tests are shown in Table 4 and Fig 2.

As the results show, the average bending strength starts from 2.6 MPa for samples without aluminum oxide, then increases to 3.6 MPa when the aluminum oxide content increases to 200 ppm. When more aluminum oxide is added (doped with) to the composition, the bending strength is decreased again to a value of 3.1

Table 3. The result of fired density of samples

Code	Fired density (gr/cm^3)	Average of Fired Density (gr/cm^3)
A1	5.22	
A2	5.21	5.2
A3	5.18	
B1	5.24	
B2	5.24	5.24
B3	5.25	
C1	5.31	
C2	5.32	5.30
C3	5.28	
D1	5.38	
D2	5.40	5.40
D3	5.41	
E1	5.43	
E2	5.46	5.45
E3	5.46	
F1	5.33	
F2	5.34	5.34
F3	5.36	
G1	5.31	
G2	5.30	5.30
G3	5.31	

Table 4. Bending strength of varistor samples

Code	Strength (MPa)	Average strength (MPa)
A1	2.63	
A2	2.65	2.6
A3	2.52	
B1	2.68	
B2	2.73	2.7
B3	2.70	
C1	2.98	
C2	2.99	3.0
C3	3.2	
D1	3.21	
D2	3.22	3.2
D3	3.19	
E1	3.55	
E2	3.59	3.6
E3	3.65	
F1	3.34	
F2	3.30	3.3
F3	3.28	
G1	3.00	
G2	3.2	3.1
G3	2.98	

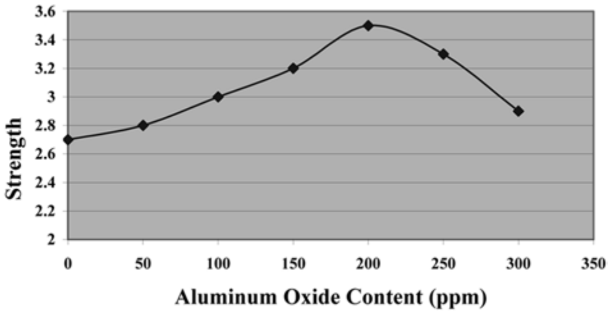

Fig. 2. The effect of aluminum oxide content on bending strength of varistors.

MPa. The value for bending strength is related to density and hardness of any material as well as to its microstructure and the distribution of defects present. The bending strength results are very compatible with density and hardness values, but one should consider the results for microstructure. Therefore, Fig. 3 shows SEM micrographs of A to G varistor samples with different Al_2O_3 contents.

The micrographs show that the porosities first decreased when aluminum oxide was increased up to 200 ppm (sample E), and then increased when the aluminum oxide contents were more than 200 ppm (sample F and, G). However, there is substantial porosity in samples, when there is no aluminum oxide in the varistor. This is due to this fact that the viscosity of the liquid phase is very small and during heating temperature up to 1200°C, the melted phase, which is passing from green pores, cannot wet ZnO particles to achieve liquid phase sintering. When the amount of aluminum oxide is increased and hence the viscosity is increased, there is sufficient time for the liquid phase to wet ZnO particles and to achieve densification, i.e. liquid phase sintering occurred completely. With an increasing aluminum oxide content and a substantial increase in viscosity, there is not enough liquid phase to wet the particles.

Table 5. α-value of sample with variable of Al_2O_3 contents

Nonlinear (α)	Code
35	A
38	B
42	C
46	D
50	E
40	F
30	G

The more α, the more differences in I and V in I-V curves, so the linearity of I-V curve is improved. Table 5 shows the α-value of samples with variable Al_2O_3 contents.

As the results show, increasing Al_2O_3 up to 200 ppm, increases the conductivity of ZnO by substitution of Al^{3+} to Zn^{2+}, which yield more vacancies in the ZnO structure. Adding more than 200 ppm Al_2O_3, forces ZnO to be conductive and the nonlinearity coefficient (α-value) starts to decrease.

As a result, the incorporation of Al_2O_3 was confirmed to improve the nonlinear properties saliently. The improvement in nonlinearity and higher I-V upturn point in samples containing a small amount of Al_2O_3 dopant suggests that Al_2O_3 doping decreases the resistivity of ZnO grains. This is because the I-V behavior of ZnO varistors in the upturn region obeys ohmic I-V characteristics and the I-V parameters depend only on the resistance of the ZnO grains. Table 6 shows the breakdown voltage of sample with variable Al_2O_3 contents.

As is known, the breakdown voltage depends on the number of ZnO grains, which stands between two varistor electrodes. It can be clearly seen that the incorporation of Al_2O_3 greatly improved the nonlinearity properties of varistors. The breakdown voltage was greatly increased from 350 to 905 V/cm due to an increase of the Al_2O_3 content. This is attributed to an increase of the number of active grain boundaries due to the decrease of ZnO grain size with increasing Al_2O_3 content.

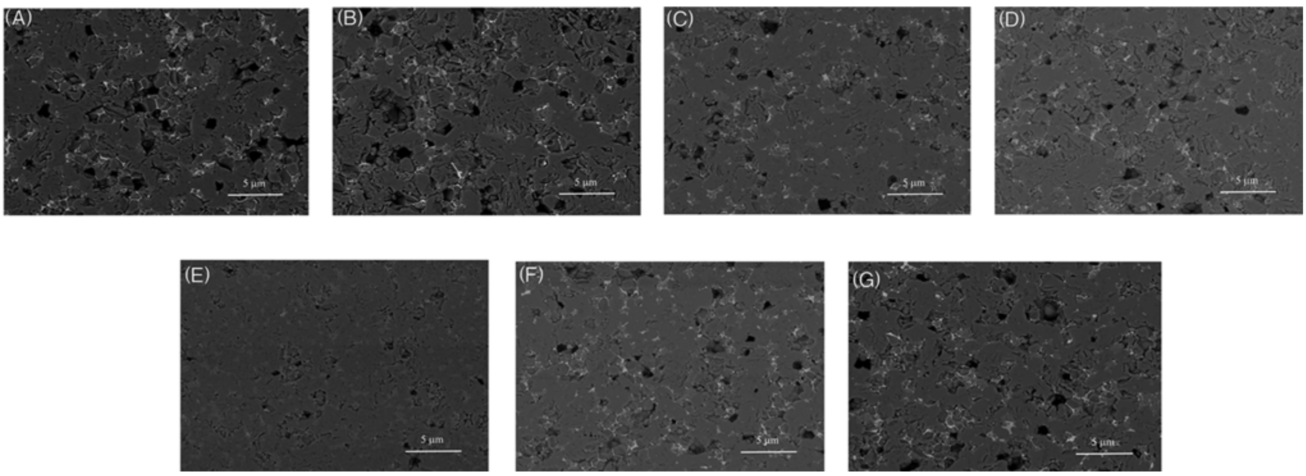

Fig. 3. SEM micrographs of the A to G varistor samples with various Al contents.

Table 6. Breakdown voltage of sample with variable of Al_2O_3 contents

Breakdown voltage (V/cm)	Code
350	A
420	B
480	C
570	D
638	E
782	F
905	G

Conclusions

In this study, different results were obtained as follows:

1. The green densities of doped varistors with Al_2O_3 was about 2.65±0.1 gcm^{-3}.
2. The fired densities was first increased from 5.2 to 5.45 and then decreased to 5.30 g/cm^3 with different Al_2O_3 content.
3. The 3-point bending strength was increased from 2.6 to 3.6 MPa and then decreased to 3.1 with Al_2O_3 content.
4. SEM evaluation showed that the porosities first decreased by increasing Al_2O_3 and then decreased.
5. The incorporation of Al_2O_3 was confirmed to improve the nonlinear properties saliently.
6. The breakdown voltage was greatly increased from 350 to 905 V/cm due to increasing of Al_2O_3 content.

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