J. Am. Ceram. Soc., **91** [7] 2402–2404 (2008)
DOI: 10.1111/j.1551-2916.2008.02436.x

Journal

Comparative Electrical Behavior at Low and High Current of SnO_2- and ZnO-Based Varistors

Miguel Angel Ramírez,[†,‡] Welson Bassi,[§] Rodrigo Parra,[‡,¶] Paulo Roberto Bueno,[‡] Elson Longo,[‡] and Josê Arana Varela[‡]

[‡]Universidade Estadual Paulista UNESP, Instituto de Química, Departamento de Físico-Química. 14800-900, Araraquara, SP, Brazil

[§]Universidade de São Paulo, USP, Instituto de Eletrotécnica e Energia. 05508-010, São Paulo, SP, Brazil

[¶]Instituto de Investigaciones en Ciencia y tecnologia de Materiales (INTEMA), UNMdP-CONILET, J.B Justo 4302, B7608FDQ Mar del Plata, Argentina

The complete *I–V* characteristics of SnO_2-based varistors, particularly of the Pianaro system SCNCr consisting in 98.9%SnO_2+1%CoO+0.05%Nb_2O_5+0.05%Cr_2O_3, all in mol%, have been seldom reported in the literature. A comparative study at low and high currents of the nonohmic behavior of SCNCr- and ZnO-based varistors (modified Matsuoka system) is proposed in this work. The SCNCr system showed higher nonlinearity coefficients in the whole range of measured current. The electrical breakdown field (E_b) was twice as high for the SCNCr system (5400 V/cm) than for the ZnO varistor (2600 V/cm) due to a smaller average grain size of the former (4.5 μm) with respect to the latter (8.5 μm). Nevertheless, we consider that another important factor responsible for the high E_b in the SCNCr system is the great number of electrically active interfaces (85%) as determined with electrostatic force microscopy (EFM). It was also established that the SCNCr system might be produced in disks of smaller dimensions than that of commercial ZnO-based product, with a 5.0 cm^{-1} minimal area–volume (A/V) ratio. The SCNCr reached the saturation current in a short time because of the high resistivity of the grains, which is five times higher than that of the grains in ZnO-based varistors.

I. Introduction

Varistors are nonlinear electroceramic devices with a microstructure consisting in conducting grains surrounded by insulating grain boundaries.[1] They are used as protective devices in distribution and energy transmission lines against voltage surges.[2] During the last 30 years a great deal of research has been done concerning basically conduction and degradation phenomena in ZnO-based varistors.[2–5] Because of their excellent nonlinear coefficients and low leakage currents, the most studied systems are those based on ZnO (Matsuoka system)[6] and the SnO_2-based system introduced in 1995 of composition, all in mol%, 98.9%SnO_2+1%-CoO+0.05%Nb_2O_5+0.05%Cr_2O_3 (SCNCr or Pianaro system).[7] The *I–V* characteristics of a varistor exhibit three main regions as indicated in Figs. 1 and 2. The relation between I and V is linear in Region I and controlled by intergranular voltage barriers.[1] Region II corresponds to the nonlinear region and stands for the protection gap of the material.[8] Finally, in Region III, at high current densities, the *I–V* relation is linear again and is controlled by the conductivity of the grains.[8] The Region III for the SCNCr varistor has been recently characterized.[9] In this paper we propose a comparative detailed analysis of every region in the *I–V* curves of the ZnO-based and SCNCr systems.

Several advantages have been reported for the SCNCr system over the commercial ZnO-based varistor. These advantages seem to be intimately related with the simple microstructure of the former, with the low concentration of additives necessary to attain electrical nonlinearity,[7] with the high refractivity of the oxides used, which minimizes losses due to evaporation,[10] with the high thermal conductivity (0.5 $W \cdot (K \cdot cm)^{-1}$) which almost doubles of that of ZnO[11] and with the excellent mechanical properties.[12] All these features determine the behavior of the material; for instance, according to recent results,[12] the SCNCr system has proven highly stable against degradation phenomena. Therefore, the electrical and microstructural properties of the SCNCr system make it an interesting candidate to substitute the traditional multicomponent ZnO varistors. However, there exist some challenges for this material to be ready for lightning protection systems or lightning rods. Some of these are the study of the influence of the geometrical ratio area-to-volume (A/V)[10,13] on the non-linear properties and the analysis of the electrical response of the device at high current densities, which are the objective of this work.

II. Experimental Procedure

The studied systems correspond to the commercial ZnO-based varistor (modified Matsuoka system) of composition

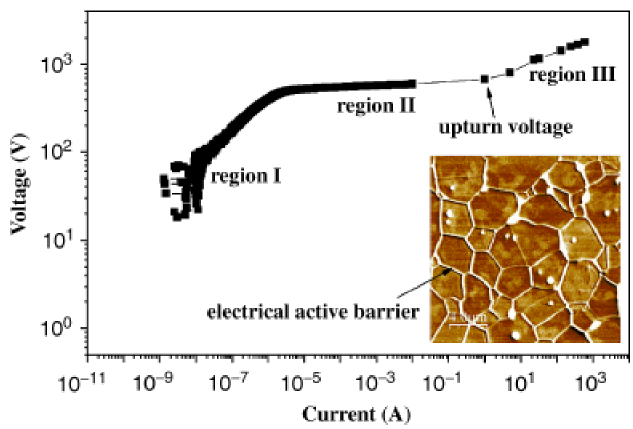

Fig. 1. *I–V* characteristics for the SCNCr system. Electrostatic force microscopy image registered with $\Delta V = 2$ V applied between the tip and the sample (inset).

M. Peiteado—contributing editor

Manuscript No. 24238. Received January 19, 2008; approved February 26, 2008.
This work was financially supported by the Brazilian financing agency FAPESP, the Industria Eletromecânica Balestro and MSc. Ronald Tararam for his assistance with the EFM measurements.
[†]Author to whom correspondence should be addressed. e-mail: margbrasil@yahoo.com
[Correction added after online publication 29 Apr 2008: Affiliations corrected.]

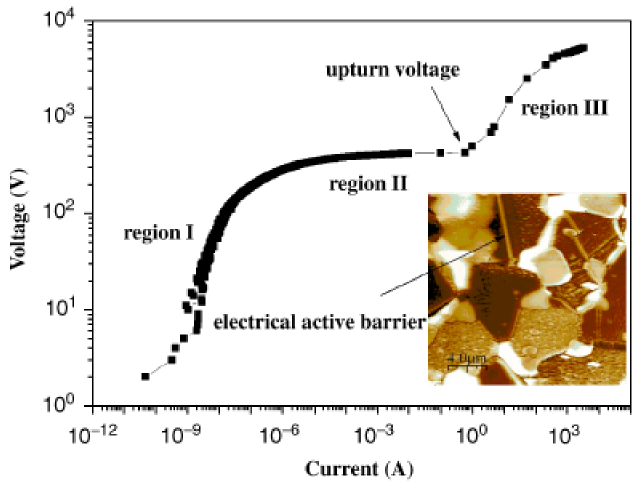

Fig. 2. *I–V* characteristics for the ZnO system. Electrostatic force microscopy image registered with $\Delta V = 2$ V applied between the tip and the sample (inset).

$95.4\%ZnO+1.5\%Sb_2O_3+1\%NiO+0.1\%SiO_2+0.5\%$ (Bi_2O_3, SnO_2, Co_2O_3, MnO) [ZnO], and to the SnO_2-based system (Pianaro system) of composition $98.9\%SnO_2+1\%$-$CoO+0.05\%Nb_2O_5+0.05\%Cr_2O_3$ (SCNCr), all in mol%. The ceramic pellets were prepared from analytical grade raw materials by mixed oxide procedures as described in previous works.[6–7,10,13] ZnO-based samples were sintered at 1180°C for 2 h, whereas SCNCr samples were treated at 1300°C for 1 h. A chamber furnace, with heating and cooling rates of 5°C/min, was used in both cases. Samples with different area–volume (A/V) ratios of the SCNCr system were prepared and the *I–V* and/or *J–E* curves registered for the most appropriate ratio. The electrical characterization was carried out on polished samples with plane and parallel faces onto which silver electrodes were deposited and treated at 400°C for 15 min.

A critical point in the finishing of the devices is the encapsulation of the ceramic disk since the selected material might influence the electrical response. In order to avoid or minimize failures of the electrical insulation, a polymeric resin resistant to high temperatures must be used. In this work, the encapsulation was done according to the following procedure:

(1) Welding of Cu–Sn wires (7 mm diameter) to the varistor electrodes.

(2) Rinsing for 10 min with deionized water in an ultrasonic bath.

(3) Drying in oven at 160°C during 30 min.

(4) Encapsulation with polyester resin (JA 022B type) warmed to 160°C. In order to cover and isolate the whole surface, the pellet must be completely submerged into the resin.

(5) Final curing at 160°C for 20 min.

The electrical parameters that determine the varistor behavior, the electrical breakdown field (E_b), the nonlinearity coefficient (α_i) and the leakage current (I_l), were obtained from *I–V* plots. The measurements were carried out at room temperature with a Keithley 237 (60 Hz) source–measure unit with a maximum current value of 10 mA, whereas high-voltage measurements were performed by means of a current generator adapted from a Haefely instrument that delivers 8/20 μs current pulses. The high-voltage circuit was based on three capacitors with total capacitance of 2.25 μF and maximum voltage and energy of 200 kV and 45 kJ, respectively. The response of the devices was registered with a Tektronix (8 bits, 100 MHz) digital oscilloscope. Because of the rapid varistor response (in the order of nanoseconds), the measurements registered with the Keithley unit can be perfectly superimposed to those obtained by pulse application.[14]

Atomic force microscopy AFM (Digital Instruments Nanoscope IIIA, Veeco, Santa Barbara, CA) in the electrostatic force (EFM) mode, with applied bias of 2 V between sample and tip, was used to study the electrical response of the grain–grain interfaces. Based on the EFM images, the amount of effective barriers (%n_e) was calculated using the methodology described previously.[15]

Table I. Electrical Parameters of SCNCr and ZnO Varistor Systems

Sample	E_b (V/cm)	V_b (V)	I_l (μA)	$d^†$ (μm)	EAI‡ (%)	$\alpha_1^§$	α_2	α_3	α_4	ρ_g (Ω·cm)
SCNCr	5400	540	1.0	4.5	85	65	25	12	11	5.0
ZnO	2600	377	1.3	8.5	35	56	11	5	5	0.9

†Average grain size. ‡Electrically active interfaces. §See text for definition of α_i.

III. Results and Discussion

The *I–V* characteristics for the SCNCr system are shown in Fig. 1. With comparing purposes, Fig. 2 shows the equivalent curve corresponding to the ZnO-based varistor. The linear ohmic region (Region I) is equivalent for both systems; the leakage current (I_l) measured at 0.80 V_b resulted similar for both systems as reported in Table I. The main difference in this region corresponds to the electrical breakdown field, which is much higher for the SCNCr system. This result is associated with a combined effect of grain size and number of electrically active interfaces. The electrically active interfaces were determined with EFM as shown in the insets of Figs. 1 and 2 for the SCNCr and ZnO varistor systems, respectively. The accumulation of charges (bright zones) observed in certain regions of the grain boundary indicates the presence of electrically active potential barriers. It was established that the 85% of the barriers in SCNCr are active, whereas only the 35% were active in the ZnO-based system. In agreement with previous reports,[16] it can be observed in Fig. 2 that twin-boundaries represent a significant contribution to the total number of electrically active interfaces in ZnO varistors. Values of electric breakdown field (E_b), average grain size (d) and number of electrically active interfaces (EAI) are shown in Table I for both systems. The calculated amount of active interfaces is consistent with recently published data for the SCNCr system[15] and confirms the goodness of the EFM technique in evaluating the active barriers in electroceramic materials. According to the literature, this technique has never been used before to characterize electrically active barriers in ZnO-based varistors. The high number of electrical barriers in SCNCr system is in turn associated with the basically monophasic and homogeneous microstructure. The fact of the SCNCr system possessing such a high number of electrically active interfaces is of great technological interest because it allows the series fabrication of varistor disks or blocks with the same V_b but with smaller dimensions than the commercial ZnO-based varistors. This will lead to the design of more versatile, more efficient, lighter, and cheaper lightning protection systems.

The possibility of fabrication of small size SCNCr varistors was confirmed by the *J–E* characteristics at low current densities for samples with equal diameters but different thickness as shown in Figs. 3(a) and (b). It is evident that samples 1 and 2 mm-thick exhibit nonlinearity. These results suggest that there exists a critical A/V ratio for the manufacturing of SCNCr varistors of 5.0 cm^{-1}, samples with values below 5.0 cm^{-1} are essentially resistive. A detailed study of the green and sintered A/V ratio can be found in Ramírez *et al.*[10] for the SCNCr system and in de la Rubia *et al.*[13] for the ZnO-based varistor. Furthermore, the length of the breakdown region (Region II) lies within the same order of magnitude for both systems (10^{-6} to 1 A). However, the transition from semiconducting to conducting occurs drastically in the SCNCr varistor. This is another advantage for this system because the ideal behavior is characterized by a rapid transition from an insulating to a conducting state.[8]

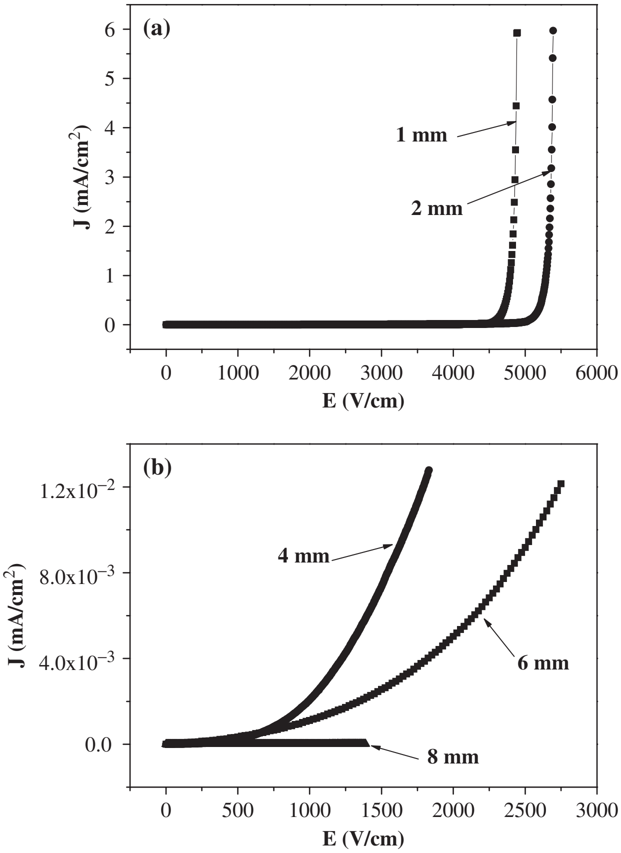

Fig. 3. *J–E* characteristics at low current densities for SCNCr ceramics with different A/V ratios. Sample thicknesses are indicated.

In order to determine the efficiency of each system, the nonlinearity coefficient was calculated in several regions of the curves: α_1 from 1 to 10 mA/cm^2, α_2 from 0.5 to 2.50 A/cm^2, α_3 from 0.5 to 50 A/cm^2, and α_4 from 0.5 to 200 A/cm^2. Then, α_1 and α_2 represent the nonlinearity coefficients for low current densities, α_3 for intermediate current densities, and α_4 for high current densities. The nonlinearity coefficients are presented in Table I as average values of three measurements. For every current density range, the SCNCr sample displayed higher values of α than the ZnO system, suggesting that the SCNCr system would be more efficient for low as well as for high current densities.

In the upturn region (Region III) the behavior is again ohmic, but in contrast with Region I where the intergranular voltage barriers control the electrical response, in Region III it is the intrinsic grains resistivity that controls the response.[1] The resistivities (ρ_g) of the grains as calculated from the slopes of the curves in Region III are also listed in Table I. Comparing the Region III for each system, it can be deduced that the SCNCr owns one disadvantage. The resistivity of the grains is five times higher than that of the grains in the ZnO system. Because of the high resistance of the grains in SnO_2-based varistors, the saturation current (10^3 A) is rapidly reached giving certain instability to the system in this region of the curve. This observation is not surprising. The SCNCr varistor is a very simple system composed by three additives only in very low concentration. As Carlson and Gupta demonstrated for the ZnO-based varistors,[14] the resistivity of the grains could be reduced by appropriate doping with donor species in order to increase the non-linear region leading to a more efficient and reliable varistor. At the moment, our research efforts are concentrated in the use of different additives in different concentrations in order to increase the stability of the SCNCr system at high current densities by decreasing the grains resistivity. Optimizing the *I–V* response in Region III, along with the design of a proper encapsulating material, would lead to a SCNCr system ready to be used in the protection of electro-electronic circuitry.

IV. Conclusions

Whole-range *I–V* curves showed that the SCNCr varistor exhibits good nonlinearity at low, intermediate, and high current densities. SCNCr varistors have shown a higher breakdown voltage than ZnO-based systems due to a combined effect that involves the smaller grain size and the higher number of electrically active interfaces (85%) of the former. This observation was associated with the microstructural homogeneity, which in turn, allows the fabrication of smaller devices. For instance, for a 20-mm-diameter disk, a thickness of at least 2 mm (equivalent to a A/V ratio of 5.0 cm^{-1}) would ensure electrical nonlinearity. Nevertheless, it is still necessary to improve the behavior of the SCNCr system at high current densities, beyond the upturn region, where the grains resistance control the electrical response.

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