Nonlinear electrical properties and stability of Zn-Pr-Co-Er-M (M = Ni, Mg, Cr) oxide-based varistors

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ZnO varistors are electroceramic semiconductor devices made by sintering ZnO powder doped with minor additives, such as Bi_2O_3, Pr_6O_{11}, CoO, and so on. They exhibit highly nonlinear voltage–current (V–I) characteristics expressed by $I = kV^{\alpha}$, where k is a constant and α is a nonlinear coefficient, which is an inherent parameter of varistors. Moreover, they possess excellent surge withstanding capability. Therefore, they have been widely utilized as the surge absorbers in electronic systems and the core elements of surge arresters in electric power systems [1, 2]. The majority of commercial varistors are Bi_2O_3-based ZnO varistors containing Bi_2O_3, which inherently induce nonlinear properties. However, they possess a few drawbacks [3] caused by high volatility and reactivity of Bi_2O_3. In recent years, Pr_6O_{11}-doped ZnO varistors have been studied to overcome these problems [4–9].

Nahm *et al.* reported that the ternary system ZnO-Pr_6O_{11}-CoO-based varistors have highly nonlinear properties when rare earth metal oxides, R_2O_3 (R=Er, Dy, Nd) are added [7–9]. To develop the varistors of high performance, it is very important to comprehend the effects of the individual additives on varistor characteristics. This paper is to investigate the influence of additives (Ni, Mg, Cr oxide) on microstructure, nonlinear electrical properties, and stability of quaternary system ZnO-Pr_6O_{11}-CoO-Er_2O_3-based varistors.

Reagent-grade raw materials were used in proportions of 97.5 mol% ZnO, 0.5 mol% Pr_6O_{11}, 1.0 mol% CoO, 0.5 mol% Er_2O_3, 0.5 mol% (Ni, Mg, Cr oxide). The mixture was calcined in air at 750 °C for 2 hr. The calcined powders were pressed into disks 10 mm in diameter at a pressure of 80 MPa. The disks were sintered at 1350 °C in air for 1 hr. The size of the final samples was about 8 mm in diameter and 1.0 mm in thickness. Silver paste was coated on both faces of the samples and ohmic contacts were formed by heating at 600 °C for 10 min. The electrodes were 5 mm in diameter.

The microstructure was examined by a scanning electron microscope (SEM, Hitachi S2400). The average grain size (d) was determined by the linear intercept method [10]. The density (ρ) of ceramics was measured by the Archimedes method. The V–I characteristics of the varistors were measured using a Keithley 237 unit. The varistor voltage ($V_{1\,\mathrm{mA}}$) was measured at a current density of 1.0 $\mathrm{mA/cm^2}$ and the leakage current (I_L) was measured at 0.80 $V_{1\,\mathrm{mA}}$. In addition, the nonlinear coefficient (α) was determined from $\alpha = 1/(\log E_2 - \log E_1)$, where E_1 and E_2 are the electric fields corresponding to 1.0 $\mathrm{mA/cm^2}$ and 10 $\mathrm{mA/cm^2}$, respectively.

The DC accelerated aging characteristics were performed under four stress states, (i) 0.85 $V_{1\,\mathrm{mA}}$/115 °C/24 hr (1st stress), (ii) 0.90 $V_{1\,\mathrm{mA}}$/120 °C/24 hr (2nd stress), (iii) 0.95 $V_{1\,\mathrm{mA}}$/125 °C/24 hr (3rd stress), and (iv) 0.95 $V_{1\,\mathrm{mA}}$/150 °C/24 hr (4th stress). Simultaneously, the leakage current was monitored at intervals of 1 min during stressing using a high voltage source-measure unit (Keithley 237). The degradation rate coefficient (K_T) was calculated from the expression $I_L = I_{Lo} + K_T\, t^{1/2}$ [11], where I_L is the leakage current at stress time (t) and I_{Lo} is I_L at $t = 0$. After the respective stresses, the V–I characteristics were measured at room temperature.

Fig. 1 shows the SEM micrographs of the varistors. It can be seen that the microstructure is very simple with only two phases regardless of additives: ZnO grain (bulk phase) and intergranular layer (second phase). It is well known that this is one of the important features in Pr_6O_{11}-based ZnO varistors [4]. The intergranular layers were Pr- and Er-rich phases, generated by segregating due to large ionic radius compared with Zn^{2+}. NiO-additive scarcely affected the density of quaternary system Zn-Pr-Co-Er-based ceramics, whereas MgO-additive greatly decreased the density. On the other hand, the average grain size decreased in the order of NiO→MgO→Cr_2O_3. NiO-additive improved the grain growth, whereas Cr_2O_3-additive inhibited it. The detailed density and average grain size are indicated in Table I.

TABLE I Microstructure and *V–I* characteristic parameters of the varistors

Metal oxide	d (μm)	ρ(g/cm^3)	$V_{1\,\mathrm{mA}}$(V/mm)	α	I_L(μA)
Without	15.7	5.69	102.4	31.8	6.5
NiO	18.6	5.68	104.1	27.0	15.8
MgO	15.8	5.50	150.0	35.1	9.7
Cr_2O_3	14.2	5.58	166.8	40.5	2.7

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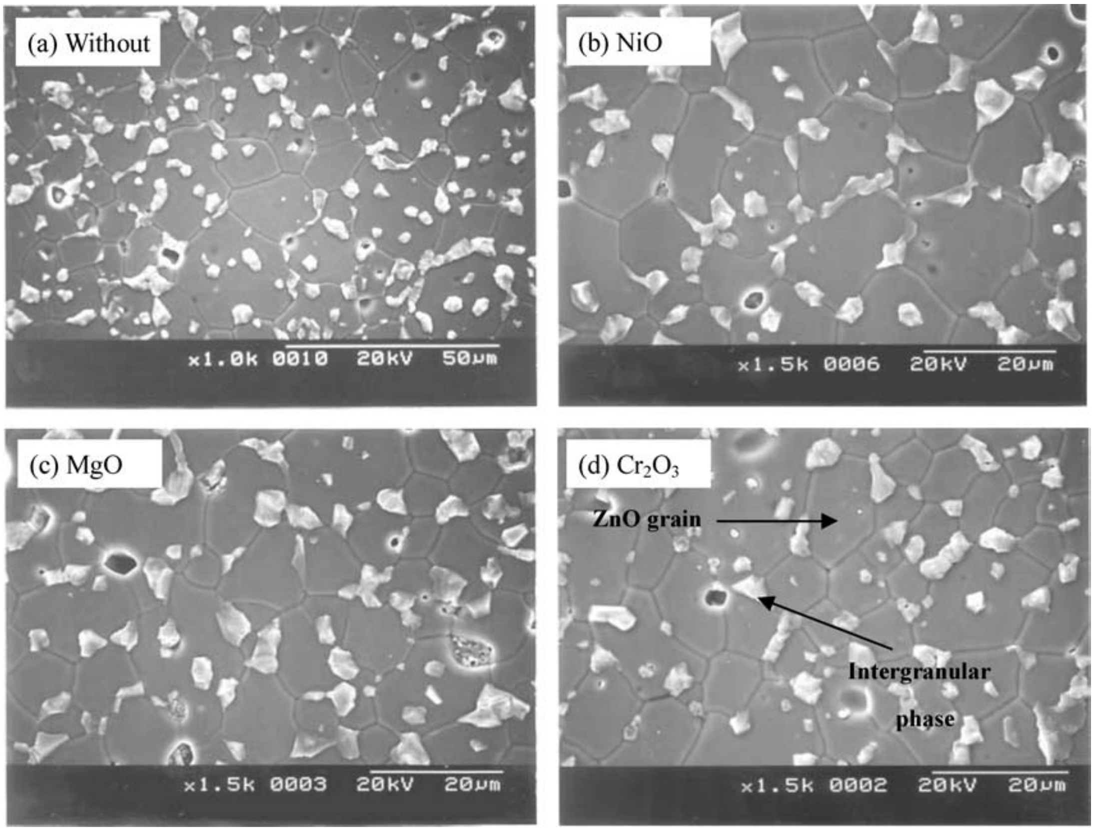

Figure 1 SEM micrographs of the varistors.

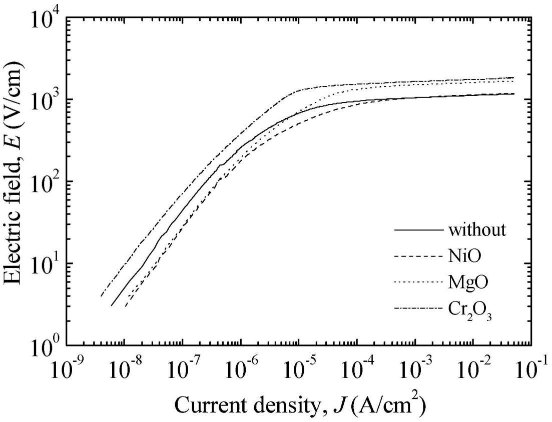

Figure 2 E–J characteristics of the varistors.

Fig. 2 shows the E–J characteristics of the varistors. The varistors show conduction characteristics dividing into two regions: prebreakdown at low field and breakdown at high field. The sharper the knee of the curves between the two regions, the better the nonlinear properties. It can be forecasted that the Cr_2O_3-added varistors should exhibit the best nonlinear properties because of the sharpest knee. For remainder additives, the knee becomes less pronounced and is close to round shape. The varistor voltage ($V_{1\ \mathrm{mA}}$) increased in the order of NiO→MgO→Cr_2O_3: 104.1→150.0→166.8 V/mm. It can be seen that this is attributed to the decrease in the number of grain boundaries caused by the decrease in the ZnO grain size. The α value was calculated to be 31.8 for the varistors without additives. The α value increased in the order of NiO→MgO→Cr_2O_3: 27.0→35.1→40.5. The Cr_2O_3-additive slightly improved the nonlinear properties, whereas NiO-additive decreased and MgO-additive scarcely affected the nonlinear properties. This show the selection of additive is very important. On the other hand, the I_L value greatly decreased in the order of NiO→MgO→Cr_2O_3: 15.8→9.7→2.7 μA. The leakage current of Cr_2O_3-added varistors was much lower than those without additives, whereas NiO-additve greatly increased the I_L value. It can be seen that the variation of I_L value shows the inverse relationship to the variation of α value. Therefore, it was confirmed that the nonlinear properties are strongly influenced by the additives.

In application of varistors, one of the important factors that should be necessarily considered is the stability of nonlinear properties. The electronic and electrical systems to be protected from various surges significantly require a high stability of varistors above all in order to enhance their reliability. In practice, ZnO varistors begin to degrade because of gradually increasing leakage current with stress time. Eventually, they lose a varistor function due to the thermal runaway. In this viewpoint, in addition to nonlinearity, the electrical stability is technologically a very important characteristic of ZnO varistors.

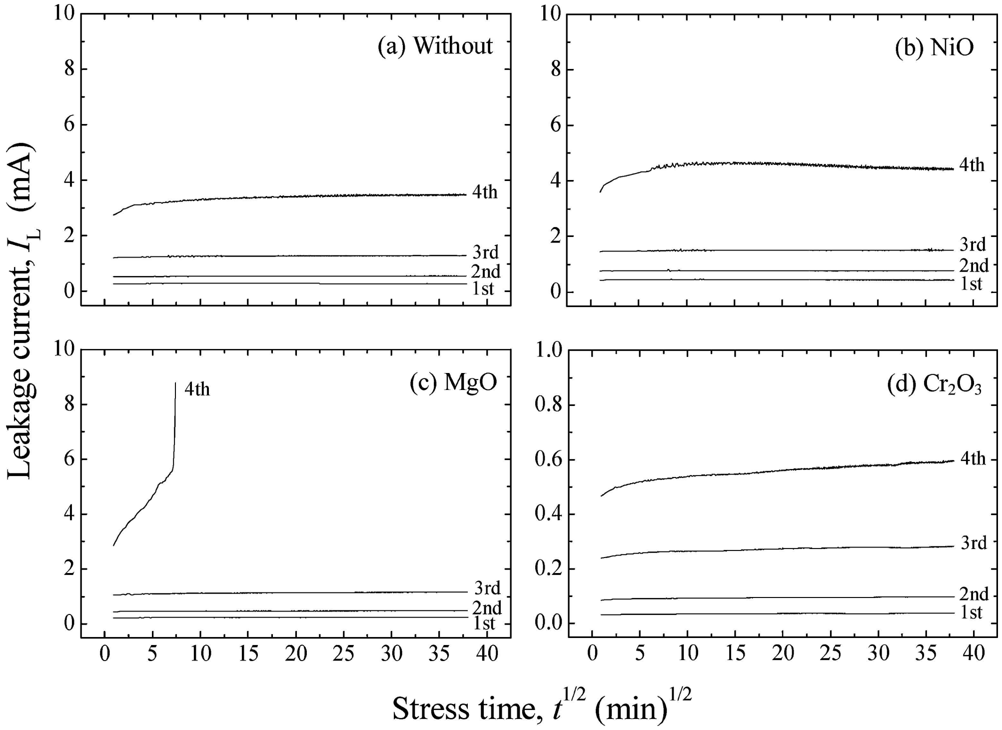

Figure 3 Leakage current of the varistors during DC-accelerated aging stress.

Fig. 3 shows the leakage current of the varistors during DC-accelerated aging stress. The MgO-added varistors exhibited a high stability until the third stress, whereas the thermal runaway within a short time, under the fourth stress. On the contrary, the varistors without additives and, NiO and Cr_2O_3-added varistors exhibited a high stability without thermal runaway until the fourth stress. The stability of varistors can be estimated by the degradation rate coefficient (K_T), indicating the degree of aging. The lower the K_T value, the higher the stability. The Cr_2O_3-added varistors exhibited positive creep of leakage current (PCLC) through entire stress states, in which the K_T value was +0.4, +1.4, +4.0, and +15.5 μA h$^{-1/2}$, respectively, with stress order. On the contrary, the NiO-added

TABLE II Variation of V–I characteristic parameters of the varistors after DC-accelerated aging stress

Metaloxide Stress state	K_T(μA h$^{-1/2)}$	$V_{1\text{ mA}}$(V/mm)	%$\Delta V_{1\text{ mA}}$	α	%Δ α	I_L(μA)	%ΔI_L
Without							
Before	–	102.4	0	31.8	0	6.5	0
1st	0.3	101.7	−0.7	30.8	−3.1	7.1	9.2
2nd	2.5	101.5	−0.9	30.5	−4.1	7.4	13.8
3rd	8.4	101.1	−1.3	29.8	−6.3	8.3	27.7
4th	53.9	100.3	−2.1	28.9	−9.1	10.6	63.1
NiO							
Before		104.1	0	27.0	0	15.8	0
1st	−2.5	103.6	−0.5	28.0	3.6	13.9	−12.2
2nd	−0.5	103.6	−0.5	28.0	3.7	14.0	−11.3
3rd	0.6	103.4	−0.7	27.6	2.3	14.8	−6.0
4th	−74.4	102.9	−1.2	26.7	−1.1	17.3	9.6
MgO							
Before	–	150.0	0	35.1	0	9.7	0
1st	0.3	149.1	−0.6	36.1	2.9	6.7	−31.1
2nd	3.0	148.9	−0.8	35.7	1.7	8.7	−10.7
3rd	12.1	148.2	−1.2	33.9	−3.6	16.1	66.1
4th	Thermal runaway						
Cr_2O_3							
Before	–	164.0	0	38.1	0	2.4	0
1st	0.4	162.5	−0.9	35.9	−5.7	3.0	26.6
2nd	1.4	161.7	−1.4	35.1	−7.9	4.5	88.2
3rd	4.0	160.4	−2.2	33.2	−12.8	6.0	154.0
4th	15.5	159.7	−2.6	30.5	−19.9	11.7	394.9

varistors exhibited negative creep of leakage current (NCLC) through entire stress states, in which the K_T value was -2.5, -0.5, $+0.6$, and -74.4 μA $h^{-1/2}$, respectively, with stress order. As a result, it can be seen that NiO-added varistors exhibited the highest stability, which is a rare case in the varistors. The low density and high leakage current greatly decrease the resistance for the stability. The former decreases the number of conduction paths and eventually leads to the concentration of current. The latter leads to repetition cycle between joule heating and leakage current. Comparing with NiO and Cr_2O_3-added varistors, the density of NiO-added varistors is larger than that of Cr_2O_3-added varistors and the leakage cutrrent of Cr_2O_3-added varistors is much lower than that of NiO-added varistors. In view of stability, it was confirmed that the density more greatly affects than the leakage current. Furthermore, the Cr_2O_3-added varistors exhibited larger variation of characteristics than varistors without additives.

Consequently, only NiO-added varistors greatly improved stability by marking $\%\Delta V_{1\ \mathrm{mA}}=-1.2\%$, $\%\Delta\alpha$ $(=-1.1\%$, and $\%\Delta I_L=+9.6\%$ under 0.95 $V_{1\ \mathrm{mA}}$/150 °C/24 hr, as shown in Table II.

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